THE MOVEMENT OF MICRON-SIZE PARTICLES THROUGH A SAND BED

A THESIS

Presented to

The Faculty of the Graduate Division

by

Jerry B. Francis Champlin

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Nuclear Engineering

Georgia Institute of Technology

December, 1967

THE MOVEMENT OF MICRON-SIZE PARTICLES

THROUGH A SAND BED

Approved:

Date approved by Chairman: Jan. 24, 1968

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ACKNOWLEDGEMENTS

The support of the Nuclear Sciences Division, Engineering Experiment Station, Georgia Institute of Technology, and the Department of the Interior, Office of Water Resources Research made this investigation possible and their aid is gratefully appreciated. The work was administered through the Water Resources Center of the Georgia Institute of Technology as authorized under the Water Resources Research Act of 1964 (P.L. 88-379). The donation of the sand by the Pennsylvania Glass Sand Company of Columbia, South Carolina, and of the clay by the J. M. Huber Company of Wrens, Georgia, aided much in bringing the research to fruition.

The author would like to express his appreciation to Dr. G. G. Eichholz for his interest, cooperation, and advice. Special thanks are due Joe K. Cochran of the School of Ceramic Engineering for the x-ray diffraction analyses, Beaufort Law of the Engineering Experiment Station for the electron microscopy, and Charles S. Cooper and Bobby Soekardiman for helping to take the data.

Special permission was received from the Graduate Division to center the page numbers so that the thesis could also be used as a report for the Water Resources Center.

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SUMMARY

The movement of certain radioactive ions and other impurities over considerable distances through underground aquifers is of great interest in those areas where control of radioactive waste and other environmental pollutants is a concern. In order to study this phenomenon, scandium-46 was adsorbed to micron-size kaolin particles dispersed in water and the suspension was allowed to percolate slowly through a horizontal packed bed of sand two meters long, one meter wide, and 0.25 meter thick which served as a model aquifer.

Continuous analyses of the effluent for particulate load, dissolved ions, and radioactivity showed that a finite fraction of the radioactively labeled particles was carried through the bed. This fraction was approximately 0.025 percent. In addition, it was possible to show by lateral scanning and vertical coring of the sand bed, after the completion of the test, that the bulk of the radioactive particles had been removed by filter action within the first 10 cm of the packed sand bed.

The experiments established that it is possible for suspended micron-size particles in flowing water to compete with the ion exchange processes on sand particle surfaces for trivalent ions, such as scandium and ruthenium, and to transport them large distances through an aquifer. This mechanism helps to explain the apparently anomalous mobility of ruthenium from reactor fuel waste disposal areas.

CHAPTER I

INTRODUCTION

In nuclear technology, movement of radioactive materials in ground- and surface waters is of particular interest in three areas:

a) disposal of radioactive wastes

b) fallout from nuclear explosions

c) radioactive tracers in pollution and environmental studies.

The largest quantities of radionuclides occur in radioactive wastes which arise from processing reactor fuel elements. The longer-lived fission products ($T_{\frac{1}{2}} > 6$ months), which may require retention or storage for some time in tanks or underground pits, are the main concern here. Among these fission products, ruthenium has shown an unexpected mobility, appearing at considerable distances from burial sites, without apparent retention by ion exchange with the cations in the soil as the other fission products are typically affected (Amphlett, 1961; Straub, 1964; Auerbach, 1963).

Some of the work done at Georgia Institute of Technology has indicated that such long-range movement may be associated with adsorption on solid particles suspended in water (Eichholz, Galli, and Elston, 1966; Champlin and Eichholz, 1968). While the transport of ions commonly is considered only in terms of solution in a mobile carrier such as water, the mechanism of ionic transport by adsorption of ions on suspended particles could be of considerable importance at trace levels of concentration.

The present work has been concerned with demonstrating that such movement by adsorption to fine, mobile particles is not peculiar to ruthenium. On the contrary, it may be possible for many other elements, especially those that form trivalent ions, in open water courses and in the restricted conditions of porous, permeable aquifers.

Interaction of Cations with Soil Particles

Cationic and Anionic Exchange

Porous, granular beds of mineral and organic residues such as soils or sands interact with cations, held in aqueous solution, by a process known as ion exchange. Commonly, this involves the relatively simple process of exchanging one ion from the solution for another which is held more or less tightly in the diffuse double-layer surrounding a micro-mineral. Since most micro-minerals are composed of silicates or some form of silica that form negatively charged particles in an aqueous environment, the ion exchange is predominantly that of cations or bases (v. Olphen, 1966). Although there also may be involvement of anions, it is small relative to that of the cations. Consequently, the term ion exchange will be used as synonymous with cation or base exchange.

Valence Dependence and Other Influential Factors

Generally speaking, the exchange reaction is dependent on the relative charge density of the ion. Hence, a monovalent cation such as sodium is held less strongly by a mineral grain than is a divalent ion such as calcium, or a trivalent cation such as lanthanum. In addition, the charge density increases somewhat with increasing atomic weight for simple ions of equal valence. One might expect, therefore, that cesium

would be held more strongly than potassium or sodium, strontium more strongly than calcium, et cetera. That this is not always the case in experimental work or in field observations on natural waters means only that other factors have considerable influence. Lawrence (1965) observed that some of these influential factors were

1) the solubility of the substrate-cation compound

2) the relative concentration of the ions in solution

3) the distribution of the attractive forces on the substrate

4) the presence of other ions in the solution that compete for the absorption sites by means of mass action

5) the presence of films of mineral, organic, or semi-soluble anion groups on the surface of the mineral particle

6) the size and electronic configurations of the ions and particles involved

7) the relationship between ion characteristics and immobilization of water molecules.

In addition, perhaps, the formation of complex chemical systems should be considered as a separate item; for the complex may act very different in the solution from either of the component parts.

The Cation and Particle Interrelationship in Moving Water

By and large, if the system can be clearly defined, the relative degree of adsorption may be expected to proceed as suggested above. Cations in a water solution slowly flowing through a bed of soil or sand would be expected to exchange with the cations on the soil particles, depending on the relative concentration of the particular ions in the two media and the contact time. The mobile cations from the solution

would then become immobilized by adsorption to the stationary soil surfaces. However, if the cation has previously been adsorbed on a fine particulate which is not a component of the porous medium but suspended in the moving fluid, then the cation is not immobilized by adsorption. Rather, it is, in a sense, only complexed and thereby less likely to enter into exchange with other soil surfaces as the water suspension flows through the soil bed. In fact, the complex formed should remain relatively stable until it comes into the presence of another chemical or solid substrate with which the cation or particle could form an even more stable complex or insoluble compound.

The Part Played by the Soil

Generally considered, radioisotopes are thought to be transported by moving water in solution until they react with the soil and become attached to an immobile medium. Nevertheless, a wide range of particle sizes of the soil are themselves mobile in the presence of a flowing fluid, becoming more so as the size or density of the particle relative to that of the fluid molecules decreases. In these cases, fine particles become dislodged by the effects of changes in the ionic strength of the water surrounding them or they may be drawn into suspension merely by the introduction of water to a dry soil, whereby they are displaced from their places of attachment. The fine particles interact with cations in the solution by adsorbing the ions onto their surfaces. Kept in suspension by the movement of the groundwater, these particles may then migrate into stream courses and drift with the current in the surface waters until the velocity of the suspending fluid drops sufficiently to allow them to settle out. Several workers have noted the asso-

ciation of radioactive elements with fine particles of soil to be a means by which these nuclides were transported in open streams or in bays (Anon., 1961; Lomenick, 1963; Bensen, 1960; Jones, 1960).

Very fine particles, less than a few microns in diameter, do not settle out very rapidly. Indeed, a particle of the density of quartz one micron in diameter, shows little inclination to settle over a long period of time. Calculations on such a system by Lapple (1951) using spherical particles of twice the density of water gave the results which are shown graphically in Figure 1. In this system, the force exerted by gravitation and that resulting from Brownian movement (as a result of thermal energies) are equal in magnitude at a particulate diameter of 1.1 micron. Use of the density of quartz instead would shift the intersection of the curves to slightly less than one micron. Use of plates instead of spheres would amplify the Brownian displacement while generally delaying the gravitational settling with the result that the intersection would shift upward, probably to approximately two microns particulate diameter.

When the Brownian motion essentially balances the tendency to settle by gravitational effects, the particle may be maintained in suspension for considerable lengths of time. In this state, the particles may move with the water through the soil as long as the physical dimensions of the flow path are sufficiently large to permit their passage. In as much as the attractive forces between the sand and the particles in suspension are of such short range as those attributed to Van der Waals effects, physical retention is more likely to be the dominant removal mechanism for particulate matter at low velocities of flow.

Interactions Between Soil and Cations Common to Radioactive Wastes

Radioactive wastes produced by processing uranium fuels that have

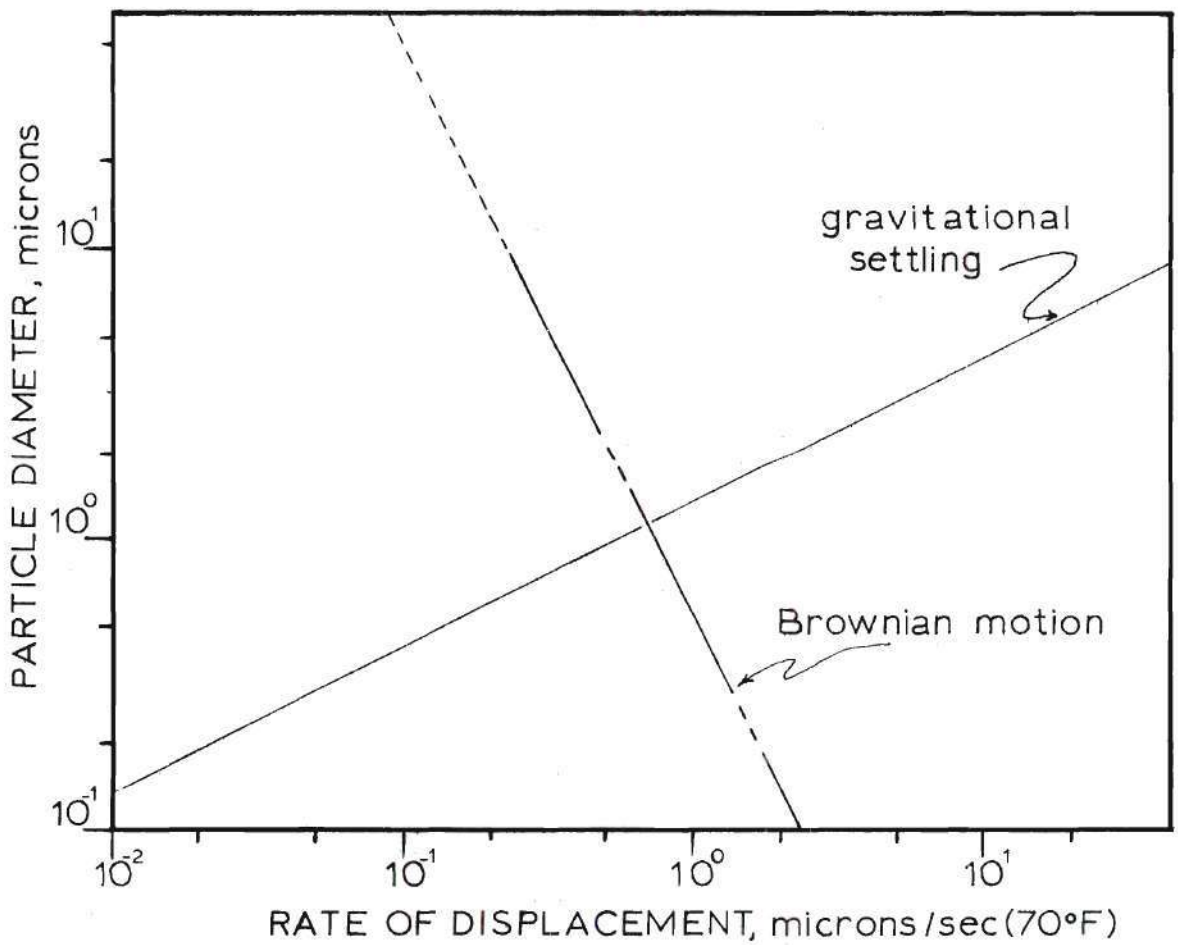


Figure 1. Comparison of the Rate of Particulate Displacement in Gravitational Settling and Brownian Motion (after Lapple, 1951)

been in storage for at least one year include some relatively long-lived products of nuclear fission such as ruthenium, strontium, and cesium. The relative degree of adsorption of the simple ions of these three elements on siliceous surfaces is essentially in the order listed. The amount of these three cations adsorbed by a sandstone was shown to have a logarithmic relationship to the valence of the ion adsorbed (Champlin, Thomas, and Brownlow, 1967). In general, one would expect that the trivalent ions of aluminum, scandium, ruthenium, and the trivalent rare-earth group would be held far more strongly by soil-forming minerals than either the mono- or di-valent ions.

Field Observations of Radioactive Element Movement

In apparent contradiction to these experimental facts is the field observation that measurable quantities of radioisotopes have been found in groundwater that has passed through large thicknesses of soil or porous rock wherever radioactive wastes are stored (Auerbach, et al., 1963; Parsons, 1962, 1963). This is the case despite experimental determinations showing the degree of interaction by ion exchange between the waste water and the soil to be such that large numbers of radioactive ions can be extracted from the water in relatively short distances. A certain quantity does pass through the soil apparently unreacted regardless of the distance involved (Amphlett, 1961; Straub, 1964).

In studies on the White Oak Creek disposal area at the Oak Ridge National Laboratory, the radioactive cation most commonly found in the water seeping from the waste pits dug into the Connasauga Shale was ruthenium. Coring studies made in the area showed strontium and cesium strongly adsorbed by the shale near the pit wall while the ruthenium was

escaping relatively freely through the walls of the pits and mingling with the surface waters of White Oak Creek (Lomenick, 1963; Auerbach, et al., 1963).

Attempts have been made to interpret this movement as being due to some complex or complexes of the nitrosyl ruthenium believed to occur in the high nitrate environment of the atomic reprocessing plants' waste streams (Fletcher, et al., 1955). However, anionic forms (even in complex states) are known to adhere to soil particles if to a lesser degree than the cationic forms (Lawrence, 1965; v. Olphen, 1966; Faust and Hunter, 1967), and some interesting research by Jones (1960) showed extensive adsorption of nitrosyl ruthenium to sediments. Perkins and Williams (1966) found radio-ruthenium, thought to have been derived from the waste effluents at Windscale, associated with ocean sediments sufficiently mobile as to be found caught in fish gill-filters and drifting with the currents off-shore in the Irish Sea and the Solway Firth. Even during experimental tests on particulate removal from large volumes of low-level radioactive process-waste at Oak Ridge National Laboratory (Anon., 1961), ruthenium was consistently found associated with the finest fractions of particulate matter.

Ruthenium as an Ion in Fuel Wastes

The chemistry of ruthenium is complex and subject to many variables which are known to affect it either in the process stream or in the environment. The element has several different valence states and, being a transition element, is subject to action as both a cation and an anion (Wyatt and Rickard, 1961). In its valence states greater than +3, it commonly forms complex ions with oxygen which are not dissimilar to

nitrate ions in their reaction with the soil. In the form RuO_4, ruthenium is quite volatile and has to be considered as a component of the gaseous effluent whenever liquid wastes are evaporated or solid wastes are calcined. In order to allay the rapid movement of the anion through soils or the volatilization of the tetraoxide, the wastes are often treated with agents which reduce the ruthenium to a lower valence. The continual presence of both oxidizing agents and reducing agents along the process stream and in the environment where the waste might be stored assures that some cationic and anionic ruthenium are present in the final product. Straub (1964) discusses the movement of both anionic and cationic ruthenium through soils at Hanford.

In the form of a trivalent cation, ruthenium movement has been noted in the field far more than other ions of equal valence for several reasons. First, in the fission reactions that take place in uranium fuel, there is no production of the more common trivalent ions such as iron, aluminum, or scandium. Second, isotopes of the lanthanide series which are commonly trivalent are produced as short-lived products for the most part. Third, the other trivalent ions that might be produced are weak radiation emitters and detection of them is generally impractical in the field.

Table 1 is a list of isotopes formed by fission reactions which have half-lives long enough to be still present in substantial quantities after one year of storage. Due to the nature of the nuclear reactions, only those isotopes which have half-lives from 0.5 to 50 years and which have sufficiently high cross-section for creation in the fission reaction will be available in any quantity in the waste material obtained by re-

Table 1. Isotopes Formed in Uranium and Plutonium Fission Reactions Still Present After One-year Storage (Taken from Templin, 1963)

Mass No.	Fission Product	Cummulative Yields, % U-233	U-235	Pu-239	Radiation Type*	Energy > 0.5 MeV	Half-Life
90	Sr	--	5.8	--	β	0.54	28 y
	(Y)				(β)‡	(2.27)	(64.2 h)
93	Zr	7.10	--	--	β	--	10^6 y
106	Ru	0.28	--	5.0	β	--	1 y
	(Rh)				(β)	(3.53)	(30 s)
127	Te	--	0.04	--	IT	--	105 d
					β	--	
	(Te)	--			(β)	(0.69)	(9.3 h)
135	Cs	> 4.9	--	5.53	β	--	2.6×10^6 y
137	Cs	7.16	6.15	5.24	β	0.52	30 y
						1.18	
	(Ba)				(γ)	(0.66)	(2.6 m)
144	Ce	4.1	6.0	5.28	β	--	285 d
					γ	--	
	(Pr)				(β)	(2.99)	(17.3 m)
151	Sm	0.27	--	1.17	β	--	80 y
					γ	--	
155	Eu	--	0.03	0.22	β	--	1.9 y
					γ	--	

*Radiation types listed only if emission intensity exceeds two percent.

‡Information in parentheses (X) refers to daughter product only.

processing the spent fuel (Templin, 1963; Straub, 1964). Note that few of the isotopes listed have a radiation with more than 0.5 MeV energy. Of these, only Sr-Y^{90}, Ru-Rh^{106}, Cs-Ba^{137}, and Ce-Pr^{144} appear to be detectable under field conditions.

Ruthenium from Fallout

Larson, et al. (1966), in discussing the fallout of Operation Plumbob (in the Plowshare program), considered ruthenium predominantly associated with particulate sizes less than 40 microns in diameter and subject to considerable transport by flowing water. More recently, Iwashima and Yamagata (1966) were able to show that such rapid transport of the ruthenium was not characteristic of radioactive waste alone, but was encountered also with fallout ruthenium where the nitrate forms, found in process wastes, were not present. They found the ruthenium to be so mobile compared to strontium or cesium that much of it was rapidly removed from the surface and washed into the oceans by the rains.

Other isotopes of cesium, strontium, and ruthenium of shorter half-life and more energetic emission are available in the first few weeks of fallout duration. However, the elemental composition of fallout is not likely to be greatly different from that of the fission product waste shown in Table 1 except for a few elements which are principally anionic, like I^{131}, or of relatively low yield in the fission reaction such as As^{77}, Sb^{127}, and Sn^{121} (Templin, 1963; Gretsushkina and Israel, 1964; Eichholz, Craft, and Galli, 1967).

The Importance of Radioisotope "Leakage" Phenomena

While the quantities of radioisotopes that migrate are relatively small compared to the bulk wastes stored (Cowser and Morton, 1959; Straub,

1959; Schultz-Rittmer, 1966; v. Liebscher, Habashi, and Schönfeld, 1961; Witkowski, 1956; Parsons, 1962), this "leakage" poses a sufficient threat to the environment to make worthwhile an investigation of the possible means by which that residual activity is transported through aquifers. Certainly, a full understanding of this long-range migration of trace ions is of primary importance in studies of the auto-purification of sub-surface waters. It also may be of considerable importance in the design of new and different tracers for following the flow of underground fluids (both water and oil), surface streams, and even fluidized materials in industrial processes.

Since the "anomalous" mobility of ruthenium through groundwater makes the hypothesis of seepage of only dissolved ions untenable, it is reasonable to assume that movement may occur by means of fine particles acting as carriers for adsorbed or complexed forms of the fission products. In order to investigate this mechanism of transport, a series of experiments were carried out in a model sand bed which simulated an aquifer. Fine particles in a specific size range were prepared as carriers of radioactive tracers. This combination facilitated the logging of the motion of the carriers as well as permitting a quantitative estimate of the portion of the labeled particles that would traverse a given length of the aquifer.

In addition to ruthenium (Champlin and Eichholz, 1968), work was done with scandium as a tracer, and it is the scandium work that forms the substance of this thesis. Scandium can be traced by means of the isotope Sc^{46}, which has a convenient half-life of 84 days and which emits gamma rays of 1.12 and 0.89 MeV. The hydrous oxides of the ele-

ment occur commonly in most residual soils; being closely related chemically to aluminum and, as a homologue, to yttrium and the rare earths, it forms a logical stepping stone to any study of the movement of the rare earths in water. Since it is not a fission product, it appears that no previous work has been done on the movement of scandium in water and the present work forms the first investigation of this subject.

CHAPTER II

THEORETICAL CONSIDERATIONS

In general, the method followed in conducting the experimental work reported in this thesis was dependent not only on the choice of materials but also on how they were to be used. Consequently, before the main body of the experimental work is presented, it is essential to establish the theoretical nature of the sand-pack, the tracer particle, and the radioactive suspension used in the sand bed. To accomplish this end, certain critical data had to be obtained beforehand to permit calculations to be made. These included the mean diameter, approximate shape, and composition of the sand grains; the weight, mean grain diameter, approximate shape and composition of the clay to be used; the composition of the radioactive solution and the distribution of radioactivity in the prepared suspension, etc. In the following discussion these data will be introduced where necessary to develop the theoretical considerations.

The Nature of the Sand Bed

The sand bed employed in this experiment was prepared from 1600 pounds of glass-quality quartz sand, so cut by washing and screening that the mean grain size peaked sharply at 330 microns grain diameter. After packing with a vibrator, the sand pack was assumed in relatively close-packed condition as a homogeneous, isotropic structure through which fluids could flow without any special hindrance except at the boundaries.

Void Volume of the Sand and the Container

The bed container was so constructed that the flow of water through the sand was approximately one ml/sec during operation with two cm of water pressure head maintained across the length of the bed with the outlet 15 cm above the bottom of the sand pack. The sand pack was 99 cm wide, 194 cm long, and 21.8 cm high (avg.) giving a total volume for the bed of 4.187×10^5 cc. Cores taken from a similar bed in a previous experiment (Champlin and Eichholz, 1968) showed the porosity to be approximately 34.4 percent. The weight of quartz sand involved in this experiment was 7.25×10^5 gm. The volume occupied by solids in the pack, therefore, was

$$\frac{7.25 \times 10^5 \text{ gm}}{2.65 \text{ gm/cc}} = 2.73 \times 10^5 \text{ cc}$$

or 65.4 percent of the total measured parameter. The porosity, then, was 34.5 percent or very close to the value estimated by analysis of the cores from the previous experiment.

In addition to the void volume in the sand pack, additional void space which is filled with water during the course of an experiment may be found in the influent and effluent doors, as well as in the manifolds, tubing, and drains. By observing the amount of water required to fill the packed bed to the outlet level and allowing for the space known to exist in the doors and wicks, etc., the most direct estimate of the total porosity of the bed itself can be made. Table 2 lists the amount of extraneous void space which might fill with water during the experiment.

Table 2. Extraneous Contributions of the Container to the Water-filled Void Volume

Contributor	Internal Dimensions cm	Void Volume cc
Input door	17 x 99 x 1.27	2,137.41
Outlet door	15 x 99 x 1.27	1,885.95
Short drain	20.258 x 50	1,012.90
Long drain	20.258 x 150	3,038.70
Inlet wick	25 x 98 x 2.54 x 80%	9,956.80
Outlet wick	25 x 98 x 2.54 x 80%	
		18,031.76 (4.76 gal)

As can be seen, the total is a little over 18 liters which is a significant amount, compared to the expected void space in the bed itself of 145 liters. Actually both figures may be a little high, since full saturation of neither the wicks nor the sand by capillary action is to be expected. As the results of the experiment show, however, it is a good approximation.

Rate of Capillary Flow

One point worth considering in regard to the bed characteristics is the rate of capillary flow. At an average throughput of one cc/sec, with the cross-sectional area of the bed contributing to the flow of

$$99 \times 21.8 \times 34.6\% = 746 \text{ cm}^2$$

the average rate of flow in the capillaries is

$$\left(\frac{1 \text{ cc/sec}}{746 \text{ cm}^2} \right) = 13.4 \ \mu\text{/sec}$$

This is small compared to the velocities attained in self-diffusion of gases at normal room temperatures. The Reynolds number may be computed for this system, according to Muskat (1937), by use of the following equation

$$R\# = dv \frac{\rho}{\eta} \qquad (1)$$

where R# is the Reynolds number and $\underline{v}$ is the mean capillary velocity. For a nominal grain diameter of $\underline{d}$ = 330 microns; density, $\underline{\rho}$ = 1 gm/cc; viscosity, $\underline{\eta}$ = 1 centipoise; and velocity, $\underline{v}$ = 13.4 microns/sec; the Reynolds number is found to be 0.0442. Flow through the capillaries in

the sand is definitely darcian and the equations developed for laminar flow in porous media are pertinent to this experiment because the onset of turbulence in capillaries is taken to occur when the number has risen to unity. Finally, it is worth noting that this capillary velocity of 13.4 μ/sec corresponds to about 0.26 miles/year. For many natural, subsurface aquifers, this would be regarded as a typical velocity.

Permeability

Several characteristics of the bed can be computed from the known porosity and the set flow rate. One of these is the permeability coefficient. This characteristic has units of area and may be computed from the following equation (Muskat, 1937)

$$k = \frac{\eta Q X}{A\ (P_1 - P_2)} \qquad (2)$$

where

k is the permeability in darcys

η is the viscosity in centipoise

Q is the volume throughput in cc/sec

X is the bed length in cm

A is the cross-sectional area of the bed in cm^2

$P_1 - P_2$ is the pressure differential across the sand bed in atmospheres

A value of 46.46 darcys is obtained for the permeability of the sand-pack, using viscosity = 1 centipoise, throughput = 1 cc/sec, bed length = 194 cm, cross-sectional area (99 x 21.8 cm) = 2158 cm^2, and a differential pressure of 2 cm of water or $2/1033.2 = 1.935 \times 10^{-3}$ atmospheres.

Mean Hydraulic Radius

This calculated value of permeability combined with the established value of porosity in the Carman-Kozeny equation gives the mean hydraulic radius (Muskat, 1937) of the sand bed.

$$m = \frac{1-\Phi}{\left(\frac{\Phi \times 10^3}{5k}\right)^{\frac{1}{2}}} \qquad (3)$$

or

$$m = \frac{0.654}{\left(\frac{0.346 \times 10^3}{5 \times 46.46 \times 10^3}\right)^{\frac{1}{2}}} = 16.9 \text{ microns}$$

where

m is the mean hydraulic radius of the bed pores in microns

Φ is the porosity in decimal form

k is the permeability in millidarcys

5 is an arbitrary constant assigned by Carman (1937).

The constant seems to work very well in applications to unconsolidated as well as many consolidated sands (Champlin, Thomas, and Brownlow, 1967). The diameter of such a theoretical pore would be four times the mean hydraulic radius or 67.6 μ, and approximately one-fifth the diameter of the mean sand grain. The value computed for mean hydraulic radius by use of the Carman-Kozeny equation is about twice that calculated from a consideration of the limiting pore and shown in Figure 2 (8.5 microns). The relatively larger estimate of the Carman-Kozeny equation is obtained from considering the flow along a mean pore which is inherently larger than the limiting pore chosen for the other calculation. Whichever is used as a guide, it is still obvious that the mean passageway dimensions in the sand bed are on the order of 100-200 times the particle diameter of the

clay used in the experiment (mean diameter = 0.37 μ).

Capillarity and Sub-Saturation of the Upper Level

Since the water input and outlet were at 15 cm above the bottom and approximately seven cm below the upper surface of the sand bed, there is a relatively large portion of the bed which must adsorb water by capillary action. Movement through this section of the sand bed must inherently be somewhat different, at least at the outset, from that through the rest of the bed. It is of interest here to inquire how high water will rise in a packed bed of this type.

Assuming the interfacial angle between the quartz and the water to be 0°, then the equation for capillary rise

$$h = \frac{2 \Gamma \cos \theta}{r \rho g} \tag{4}$$

can be applied to solve for the height, h, of capillary rise. In this application h is the height of capillary rise above the mean water level in the input and outlet manifolds, $\cos \theta = 1$, Γ is the interfacial tension of the water-air-quartz system or about 73 dynes/cm, ρ is the density of water, g is the gravitational constant, and r is the effective capillary radius, which can be approximated by doubling the mean hydraulic radius. In addition to the method shown by equation (3), the latter also can be calculated by dividing the fractional void volume (porosity) of the bed by the specific surface area

$$m = \frac{\Phi}{S_a} \tag{5}$$

$$m = \frac{0.346 \text{ cc}}{181.8 \text{ cm}^2} = 19.05 \text{ microns}$$

yielding a value which is slightly larger than that calculated by the Carman-Kozeny equation. Using this value because of the conservative estimate it will give for the capillary rise

$$h = \frac{2 \times 73 \times 1}{2 \times 19 \times 10^{-4} \times 980} = 39.2 \text{ cm}$$

With this much rise inherent in the water-sand combination, it is obvious that the sand will saturate itself with water if $\cos \theta = 1$ (equation (4)). Even if a maximum probable pore radius is taken to be that of one sand grain (i.e., 165 microns), a 4.5 cm rise would be possible. This latter rise, in combination with the two cm pressure head, would essentially reach the surface of the sand on the input end and be only slightly below it on the outlet end of the bed.

Figure 2 illustrates a cross-section taken through a group of particles, assumed to be quartz spheres, in close-packed, hexagonal array. While not an absolutely true picture of a randomly selected micro-section of the sand bed, it is a good approximation for the purposes intended here and does permit calculations of the limiting values which the data in the experiment tend to verify. If the mean hydraulic radius of the triangular pore shown in the figure should be the source of the capillary driving power, the lift would amount to 88 cm, or nearly a meter. The actual value probably lay somewhere near that calculated for the 19-μ pore radius. For continuous-film development through the interstitial capillarity, an even

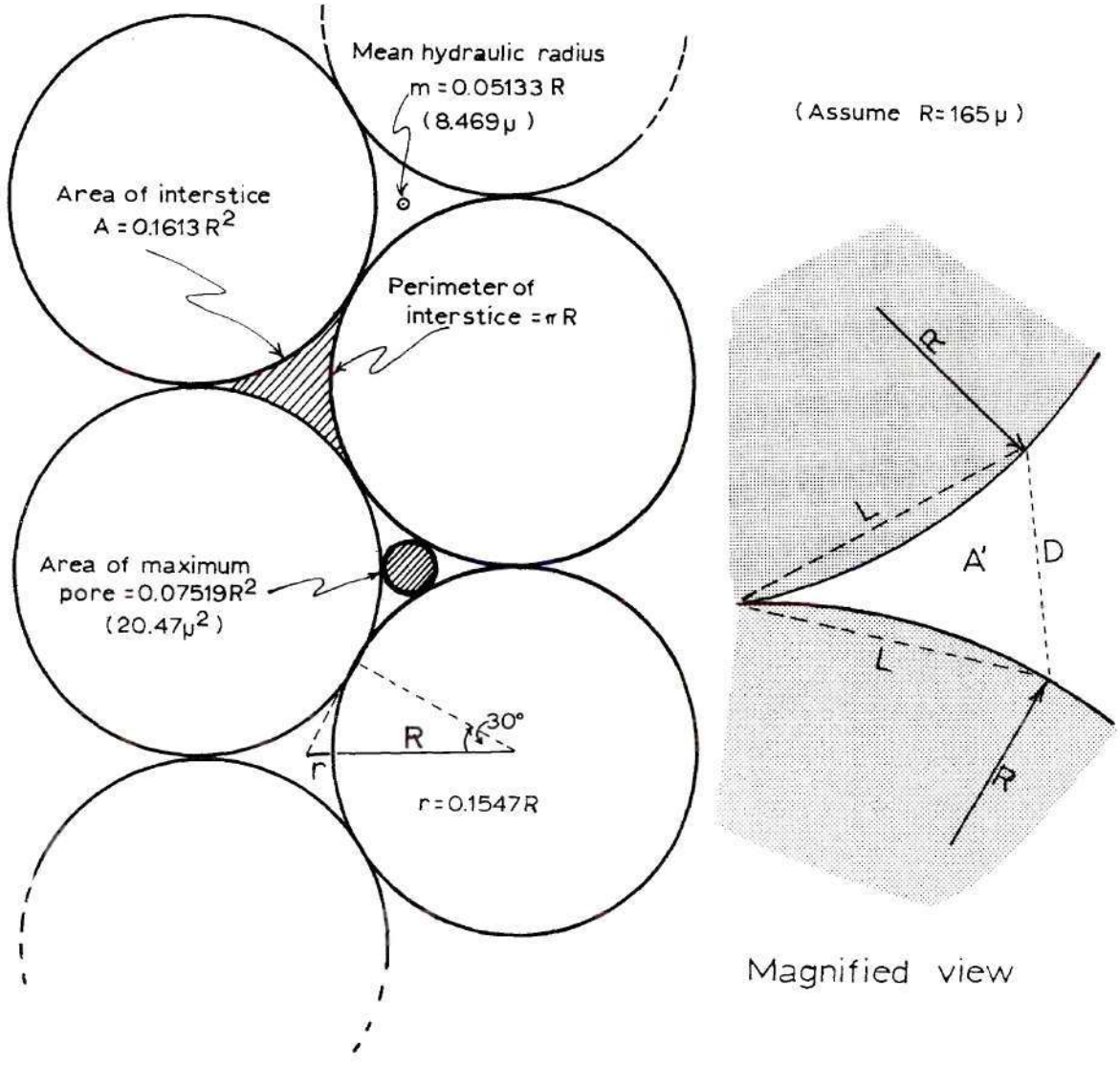


Figure 2. Critical Dimensions in a Theoretical Close-Pack of Equivalent Spheres

higher value of rise would be expected. Consideration of such a system where the capillaries are filled with air and their walls are wet with water is not pertinent to this experimental set-up, however.

Large Particle Removal by the Sand Pack

The section shown in Figure 2 is taken through the contact points of a number of grains to illustrate the interstices left between them. With close packing, these interstices may assume two shapes, the triangular one shown and a quadrilateral one that is not as common. The frequency of recurrence of the triangular arrangement is such that, in a bed of grains of roughly equidimensional shapes, it is the controlling pore-shape. In a bed of grains that are equidimensional and essentially of equal size, it is possible to calculate the dimensions of the maximum spherical particle that can pass through such a pore. The area of this maximum circular pore space, therefore, bears a definite relationship to the dimensions of the grains themselves. A calculation of this value is shown in the figure for spherical grains of 330 μ mean diameter to give 20.47 μ^2.

The upper size limit for a particle to pass through the openings described above would be on the order of 5 μ diameter. Unless the dilution was great and the particles were impelled to pass through the pore singly, the number of particles of this size passing through a bed (of the dimensions used in this experiment) would be quite limited. This triangular pore which is statistically prevalent in a close packed sand would act to provide a fixed limit to the maximum particle size that could be passed through the bed.

Small Particle Removal by the Sand Pack

While it is clear that particles larger than this limiting pore size are going to be quickly removed from an influent stream, some additional comments are necessary in regard to smaller particles. One might expect that any smaller particles passing through the channels between the grains would have no problems in traversing the entire bed except where several might enter a given capillary at one time. Hall (1957) pointed out, however, that the smaller particles can be caught in the crevices between the grains and be removed from the moving suspension by "interstitial straining" action. At the right in Figure 2 is a drawing depicting the interface between two grains with chords drawn across the arcs subtended by two grain radii. With the sides of this V-shaped wedge approaching each other in a continuous relationship, any conceivable-size particle could become entrapped.

Statistically, in a homogeneous bed in which isotropic flow takes place, the particle load in an influent stream not only would be strained so that particles larger than five microns could not pass but also an exponential depletion of the remaining particles would occur at rates that are directly proportional to particle size. If one compares the concentration of particles of a given size still in suspension at some point in the sand bed with the concentration of particles in suspension initially, the depletion or change in concentration can be represented by the following differential relationship

$$\frac{dC}{dx} = -wC \qquad (6)$$

where C represents the concentration of particles in numbers or weight units per unit volume, x is the distance of penetration into the horizontal bed of sand, and w is a rate factor that is, in essence, a removal coefficient. As Hall notes, this rate factor is seen to vary with particle size but not with position in the filter as long as the conditions of homogeneity and isotropy are approximated. With the low concentrations used in this experiment, these conditions were met throughout the study.

Integrating the differential gives the following equation that shows the exponential relationship to be expected between concentration and distance of penetration into the bed

$$C = C_o e^{-wx} \tag{7}$$

Using Hall's considerations, O'Melia (1963) offered the following equation for the approximation of the rate factor per unit length, w

$$w = \left(\frac{D}{d}\right)^{\frac{3}{2}} \frac{X}{d} \tag{8}$$

where D is the effective diameter of the influent particle, d is the effective mean diameter of the grains forming the bed, X is the total length of the bed or some functional fraction thereof (>>> d). Combining equations (7) and (8), it is possible to obtain an approximate value for the diameter of the particles being trapped if the concentration-distance relationship can be determined.

Obviously, any factors making the rate factor w small will increase the degree of transport of the particulate matter through the sand bed.

With the interstitial flow too low to cause turbulence, so that impingement effects are negligible as a particle removal mechanism, and particle sizes not large enough to make weight and gravitational sedimentation significant factors, it is clear from Hall's work that interstitital straining probably will be the dominant factor in particle removal expected in this experiment.

Effective Surface Area of the Sand Pack

The effective surface area for a bed of this size can be estimated by calculation. When the size distribution of the grains is essentially log-normally distributed, the mean diameter can be employed in calculating volume and surface area (Orr, 1966; Cadle, 1965). This diameter for the sand in this experiment is 330 μ.

The surface area of a 330 micron diameter sphere is

$$S = \pi d^2 = 342 \times 10^{-12} \text{ m}^2/\text{particle} \qquad (9)$$

Since one gram is equivalent to 0.377 cc of quartz and the volume of an individual quartz sphere is

$$V = \frac{\pi d^3}{6} = 18.8 \times 10^{-6} \text{ cc} \qquad (10)$$

The number of particles per unit weight is

$$\frac{0.377 \text{ cc/gm}}{0.188 \times 10^{-4} \text{ cc/particle}} = 2.005 \times 10^4 \text{ particles/gm}$$

On the basis of a larger quantity, since each particle has a surface area

of 3.42×10^5 square microns, there are

$$2.005 \times 10^4 \text{ part./gm} \times 10^6 \text{ gm/tonne} \times 3.42 \times 10^5 \ \mu^2/\text{part.}$$

$$\text{or } 6.86 \times 10^{15} \ \mu^2/\text{tonne}$$

Available Adsorption Sites

Considered from the standpoint of potential adsorption sites for the tracer used in the experiment, scandium-46 with its ionic radius of 0.81 Angstroms (Sc^{+3}), there are

$$\frac{6.86 \times 10^{23} \ \text{Å}^2/\text{tonne}}{2.06 \ \text{Å}^2/\text{ion} \ (Sc^{+3})} = 3.33 \times 10^{23} \text{ sites/tonne}$$

to which nearly 0.5 mole of scandium might potentially adsorb.

Not all of the surface area is capable, however, of attracting and retaining cations. If it is assumed that the surface area available for ion adsorption on the grains of quartz is on the same order of spacing as that observed for the kaolin reported by Irani and Callis (1963), then the total exchange capacity of the bed would be rated (assuming $\frac{3}{4}$ tonne) at

$$\frac{3.33 \times 10^{23} \times 0.75}{33.2} = 75 \times 10^{20} \text{ atom-equivalents}$$

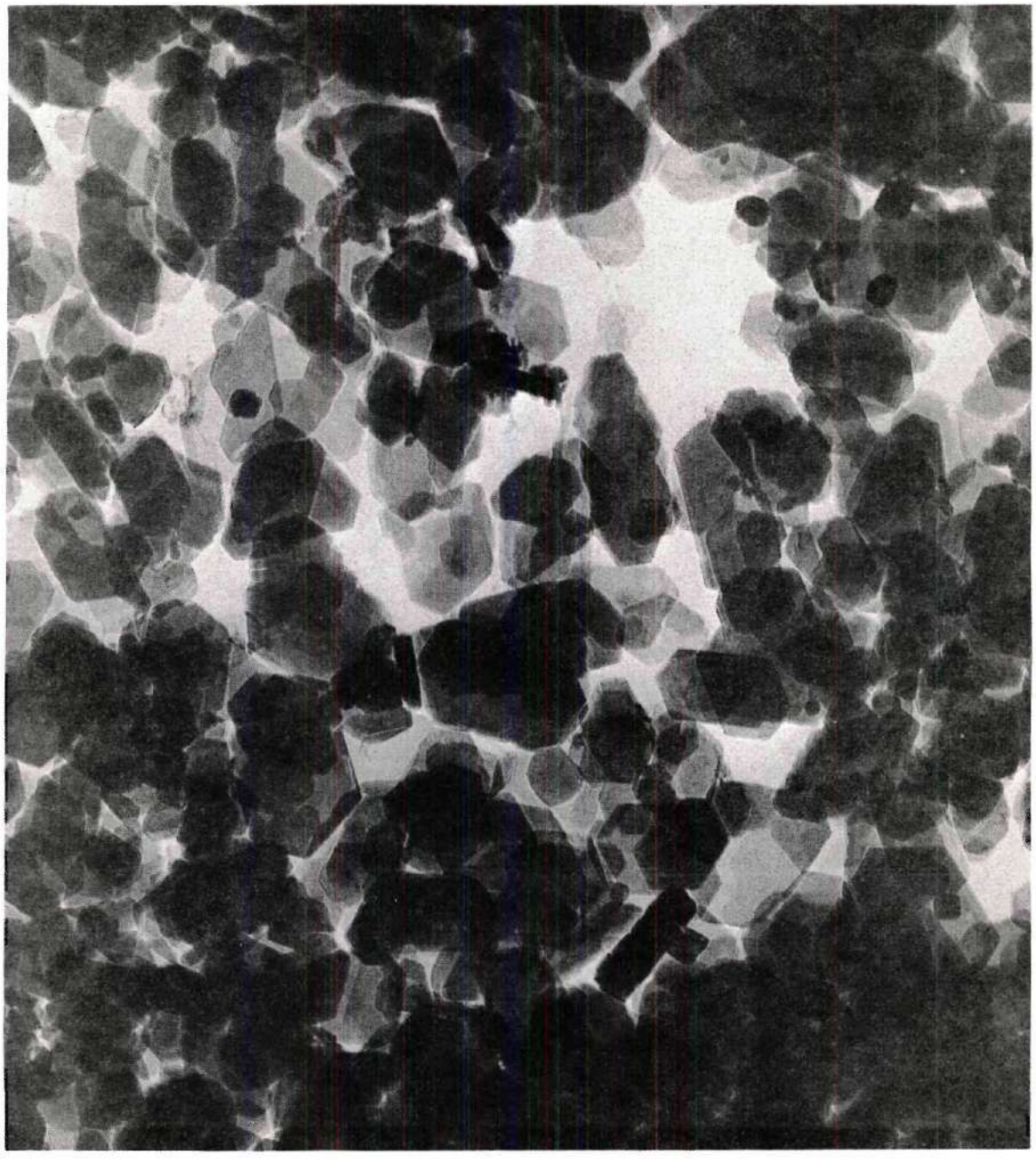
or about 75 milli-equivalents exchange capacity. Assuming comparable exchange parameters, therefore, the silica bed can be taken as equivalent to about 1500 gm of kaolin in its adsorptive capacity.

The Nature of the Tracer Particles

A special grade of fine-grained kaolin was selected for use as the

source of the tracer particles. Noting that the Company supplying the clay was having difficulty getting the particles in their processing plant effluent to settle out in large open ponds, a sample of the water suspension was obtained, thoroughly shaken and allowed to settle for about two months. The supernatant was then decanted and mixed with enough radioactive Sc^{46} to tag the particles individually. This suspension then was filtered through a 0.45 μ and then through a 0.1 μ membrane filter. The radioactivity determinations which followed showed almost no activity on the 0.45 μ filter or in the filtrate; but a large amount was found on the 0.1 μ membrane filter. This result suggested that the clay left after settling might have peaked in size-to-weight ratio near that of the 0.2 μ diameter particles. Examination of the 0.1 μ membrane filter with the electron microscope showed that this was indeed the case. An electron micrograph of some of the clay particles is shown in Figure 3. An x-ray diffraction analysis was made on the clay caught on that filter also. It was identified as kaolin with no significant admixtures of other minerals. The diffraction spectrum of the clay is shown in Figure 4.

Examination of the individual particles in the electron micrographs showed them to be nearly equidimensional, hexagonal plates with transverse dimensions about 1/30th the lateral dimensions. The most common length of a side of an individual hexagon was on the order of 0.1 μ. The larger particles were either several hexagons adhering to one another by crystal bonds along the edges of the crystals or stacks of individual plates with a total thickness about equal to the length of one of the hexagon sides.



0.1μ

Figure 3. Electron Micrograph of Kaolin Particles Used as Tracer Carrier

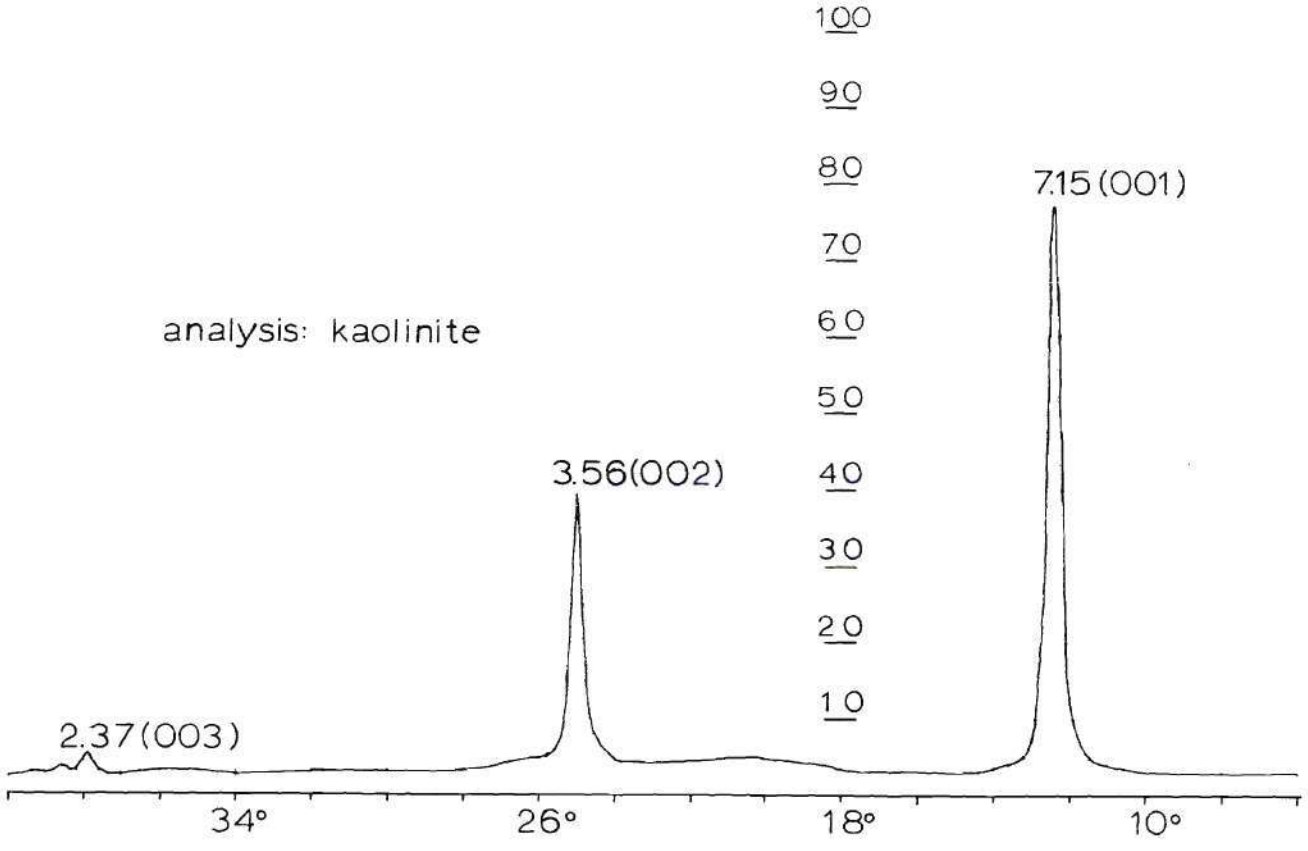


Figure 4. X-ray Diffraction Spectrum of Kaolin Used as Tracer Carrier

Surface Area

With the main surface area of the hexagonal plates (top and bottom) taken to be

$$A = 6a^2 \sqrt{3} \tag{11}$$

where a is the length of one side, the area per particle for a = 0.1 μ is 0.1039 μ^2, exclusive of the area of the edges. The latter can be calculated by

$$A_e = \frac{6a^2}{30} \tag{12}$$

to be 0.002 μ^2 per particle. The total surface area of one of these particles would be approximately 0.106 μ^2 with the edges contributing only about two percent of that total.

Potential Adsorption Sites

The volume of these individual plates is

$$V = A\ t \tag{13}$$

or 0.0035 μ^3 per particle, where t is the thickness of the individual flake ($\sim \frac{a}{30}$). At 10^{-12} cc/μ^3 and a kaolin density of 2.65, the weight per particle is found to be 198.6×10^{-16} gm. The number of particles per gram, therefore, is 5.04×10^{13}. The potentially available surface area of these particles is 53.3×10^{11} μ^2 per gram.

If the clay is assumed initially to be in the sodium state, the number of atoms that could be transported as adsorbed ions can be computed. Taking the sodium ion to be spherical with a 0.95 Å radius, it has a cross-sectional area of 2.83 Å^2. With a total surface area of 53.3×10^{11} μ^2 or

53.3×10^{19} Å^2, this represents 18.8×10^{19} potential sites to which sodium might be adsorbed per gram of clay. This amounts to about one-third millimole of sodium per gram of clay as a maximum. Generally accepted values in the literature, however, are about 0.05 millimole per gram of kaolin. Comparing these two values, it may be concluded that the adsorbed ion occupies, on the average, about six potential sites at one time. Another way of stating this is that only one potential site in six can hold an ion in an adsorbed state.

Nuclear Activation

A sample of the clay was mixed with water and allowed to settle until the supernatant liquid was only slightly cloudy, requiring several weeks of quiet, undisturbed conditions. An aliquot of the supernatant suspension was placed in the Georgia Institute of Technology Research Reactor for approximately 120 hours of neutron irradiation to determine what elements might be found in the clay in trace quantities or adsorbed to its surfaces. The only element detected with a half-life exceeding a few minutes was sodium. Figure 5 shows the gamma-ray spectrum of this clay sample. Using the integrated counts under the peak labeled 1.37, a total of about 5×10^{15} sodium atoms per gram of clay were accounted for. It should be noted, however, that this is only an approximate figure, since the irradiation was not continuous. In addition, the reactor had been shut down overnight before the sample was removed, making the assumption of t_o, the beginning of the decay time interval, rather speculative. The clay was irradiated as the suspension and the latter flocculated during the stay in the reactor. No attempt was made to homogenize the sample after irradiation. Hence, the sodium estimate given above is probably low. Nonetheless,

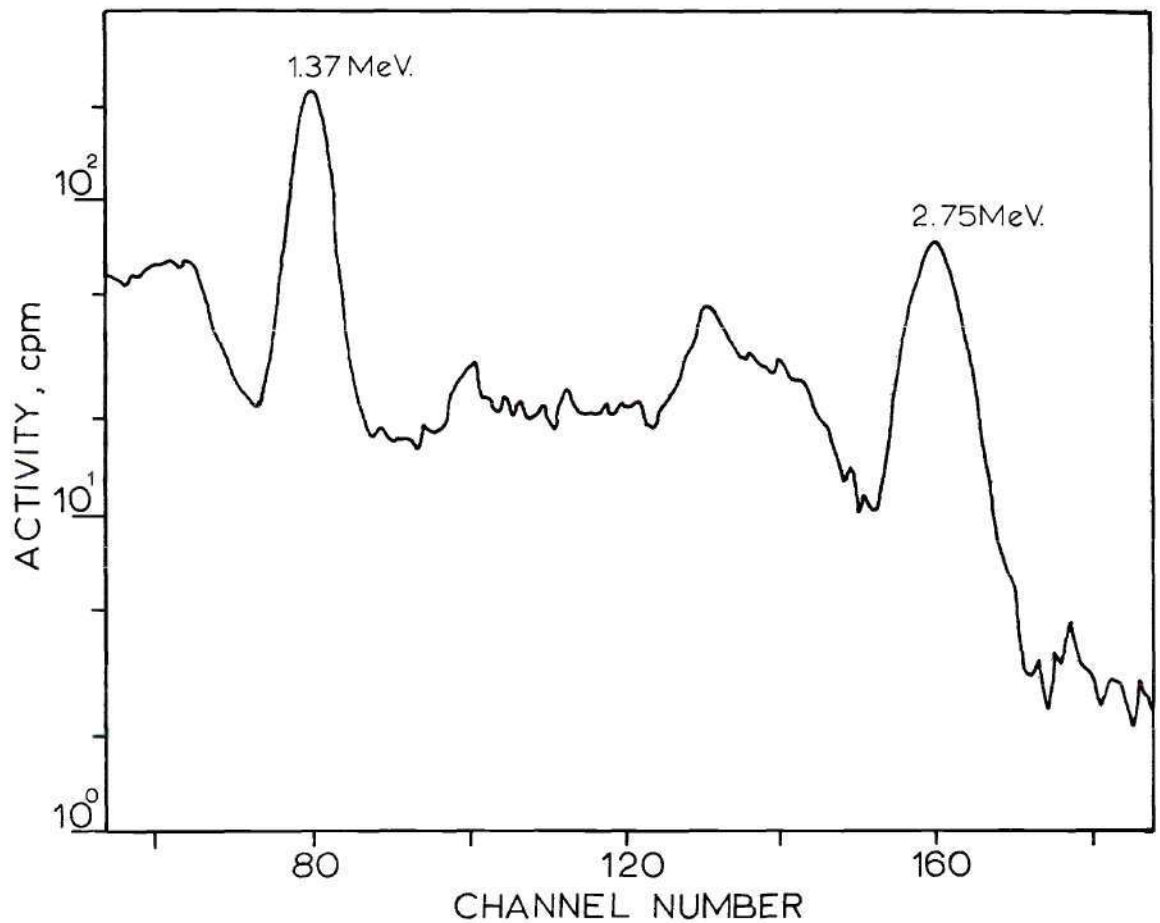


Figure 5. Gamma-Ray Spectrum of Thermal-Neutron Activated Kaolin after Cooling Overnight

with 2×10^{20} adsorption sites per gram, the clay did not appear to be saturated with sodium or with any other common cation that could be detected by thermal neutron activation.

Irani and Callis (1963) published data, shown in Figure 6, from which estimates of surface area and exchange capacity can be made. The nominal particle size considered for this experiment would have a surface area of 10×10^{20} $Å^2$/gm and an exchange capacity of 0.05 milliequivalent (meq) /gm. Considering that a large number of the possible adsorption sites are already occupied by hydrogen or aluminum ions (from the Company refining processes), the sodium figure of about 10^{16} sodium atoms per gram of clay may not be greatly out of line.

The Effect of Valence on Adsorption

The Gouy theory predicts, according to van Olphen (1966), that the ratio of the concentrations of two ions will be the same (in the diffuse double layer) on the clay as in the surrounding solution if the ions have the same valence. For ions of different valence, the ion with the greater valence is predominantly accumulated near the clay surface. Taking the basic idea of the Gouy theory and modifying it with the exponential relationship between adsorption and valence suggested by published data on consolidated rock materials (Champlin, Thomas, and Brownlow, 1967), one obtains the following equation

$$\frac{C_{Na}}{C_{Sc}} = \frac{C'_{Na} e^{(u_{Sc} - u_{Na})}}{C'_{Sc}} \qquad (14)$$

where C is the concentration in the solution, C' is the concentration on

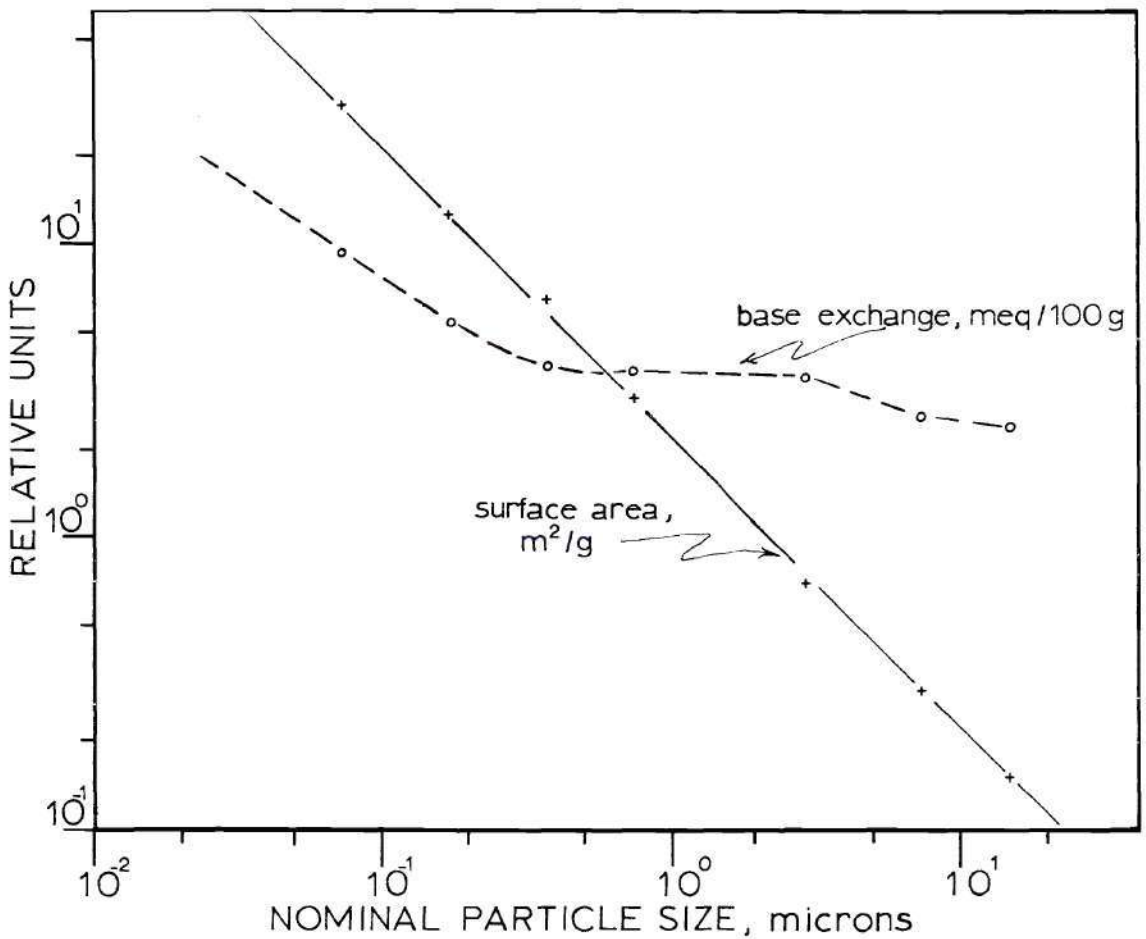


Figure 6. Kaolin Base Exchange and Surface Area Distribution Relative to Particle Size (after Irani and Callis, 1963)

the clay, and u is the valence of the respective ions.

The Probable Distribution of Sc^{46} Ions on the Tracer Particles

In preparing the kaolin used in the experiment, sodium carbonate was used as a dispersant. The excess concentration of sodium ions available in the solution over that shown by nuclear activation to be present on the clay was approximately

$$\frac{4 \times 10^{22}}{10^{16}} = 4 \times 10^{6}$$

which should have been sufficient to transform most of the clay into the sodium form, if it was not already.

The composition of the radioactive solution included other ions in relatively large amounts, included principally to keep the scandium in solution and to deter ion exchange of the tracer with the glass shipping container. The ion content determined from the assay of the solution by the manufacturer is shown in Table 3.

In mixing a dilution of that radioactive solution with the clay-Na_2CO_3 dispersion, it is obvious that the sodium and carbonate were in considerable excess. After reacting with the acid from the radioactive solution carrier and such hydrogen ions as may have been displaced from the clay adsorption sites by the excess of the sodium, 98 percent of the carbonate would still be present. Should all of the potential sites on the clay have been occupied by sodium in this interaction, 99.96 percent of the sodium would still have been present in solution.

With the sodium content of the solution virtually constant, the ratio of scandium ions to sodium ions adsorbed on the clay can be deter-

Table 3. Ion Content of the Radioisotope Solution

Ion	Valence	Number of Atoms
Scandium-45	+ 3	3.3×10^{18}
Scandium-46	+ 3	1.0×10^{15}
Hydrogen	+ 1	8.1×10^{20}
Chloride	- 1	8.2×10^{20}

mined by equation (12) as follows

$$\frac{C'_{Sc}}{C'_{Na}} = \frac{3.3 \times 10^{18}\ e^{(3-1\ =\ 2)}}{3.9 \times 10^{22}} = 6.25 \times 10^{-4}$$

Thus, out of every 1600 potential adsorption sites on the particles, one would be occupied by a scandium ion. Using the mean areal distribution of 33.2 $Å^2$ per ion on kaolin and the value of 104×10^5 $Å^2$ per particle, there would be approximately 3.14×10^5 sites for adsorption per particle. Multiplying this number by the above probability that some portion of this total will be occupied by scandium ions gives the following result

$$3.14 \times 10^5 \times 6.25 \times 10^{-4} = 196.25 \ \frac{\text{ions } (^{45}Sc^{+3})}{\text{particle}}$$

As indicated in Table 3, there were about 3000 stable scandium ions (Sc^{45}) for every radioactive ion (Sc^{46}). This suggests that the final distribution of radioactive ions would be close to one per 15 particles of clay. Assuming the six percent of the particles that are labeled to be representative of the others in their general behavior, the presence of statistical numbers of the particles would be "announced" by the radioactivity in direct proportion to the total number present, wherever they might be.

CHAPTER III

EXPERIMENTAL PROCEDURE

Since the purpose of the experiment was to show that fine particles could carry radioactivity through a bed of packed sand, the experimental aspects were largely concerned with the preparation of the sand bed, the preparation of the radioactively-tagged particles, the passing of the particles through the bed and the analytical procedures that were used to establish the results. Each of these procedures introduced separate considerations; they will be taken up in the following sections.

The method for preparing a porous granular bed consisted of packing 1600 pounds of dry sand in a special box with an electric vibrator, allowing it to soak slowly from one end with distilled water, and then leaching most of the soluble salts from the bed with more distilled water. The leaching was continued until the conductivity of the effluent dropped below detectable levels, i.e. below a measured 25 micromhos. A special fine-grade kaolin, obtainable commercially, was dispersed in water containing a radioactive trivalent ion of scandium, $^{46}Sc^{+3}$, and then injected or infused into the sand bed. Subsequently, more distilled water was pumped into the sand bed until the radioactivity was perceived in the effluent.

Continuous sampling and analyses for dissolved ions, particulate matter, and radioactivity were conducted to establish the chemical and physical situation in the sand bed as accurately as possible. This permitted making a comparison between the movement of the radioactivity,

particulate matter, and other ions.

In order to systematize a relatively large amount of pertinent information, the procedure is divided into four parts.

Apparatus

Sand Container

A special container was prepared to hold the sand. Figure 7 shows a side view of the apparatus prior to loading. It was an aluminum box with dimensions of 0.5 x 1 x 2 meters with hinged end doors and a removable lid. The hinged ends served as plenum chambers by mounting two $\frac{1}{4}$ inch aluminum plates together separated by $\frac{1}{2}$ inch strips of wood. The inner plate was perforated with $\frac{3}{16}$ inch holes spaced hexagonally at $\frac{3}{4}$ inch intervals. A manifold constructed from aluminum tubing was connected to the plenum chamber by fittings which penetrated the outer plate. A one-inch thick polyurethane wick was cemented to the inner perforated plate at each end to make contact between the plate and the sand. The wick served to distribute the input water evenly over the sand face and the outlet wick served to collect water from the sand face. The inner sides, bottom, and lid of the container were covered with a non-permeable neoprene sponge. The porous surfaces of the neoprene and the polyurethane served to interlock the sides of the container with the sand surface to prevent channeling between the sand grains and the smooth aluminum.

A one-inch thickness of plastic-bonded, wood-chip plywood was glued to the aluminum sides to support them. The bottom was supported by one inch of marine plywood backed up by a one-inch layer of wood-chip plywood. A girder system of I-beams and angle iron beneath assured a rigid supporting framework capable of withstanding a possible load of up to two tons with

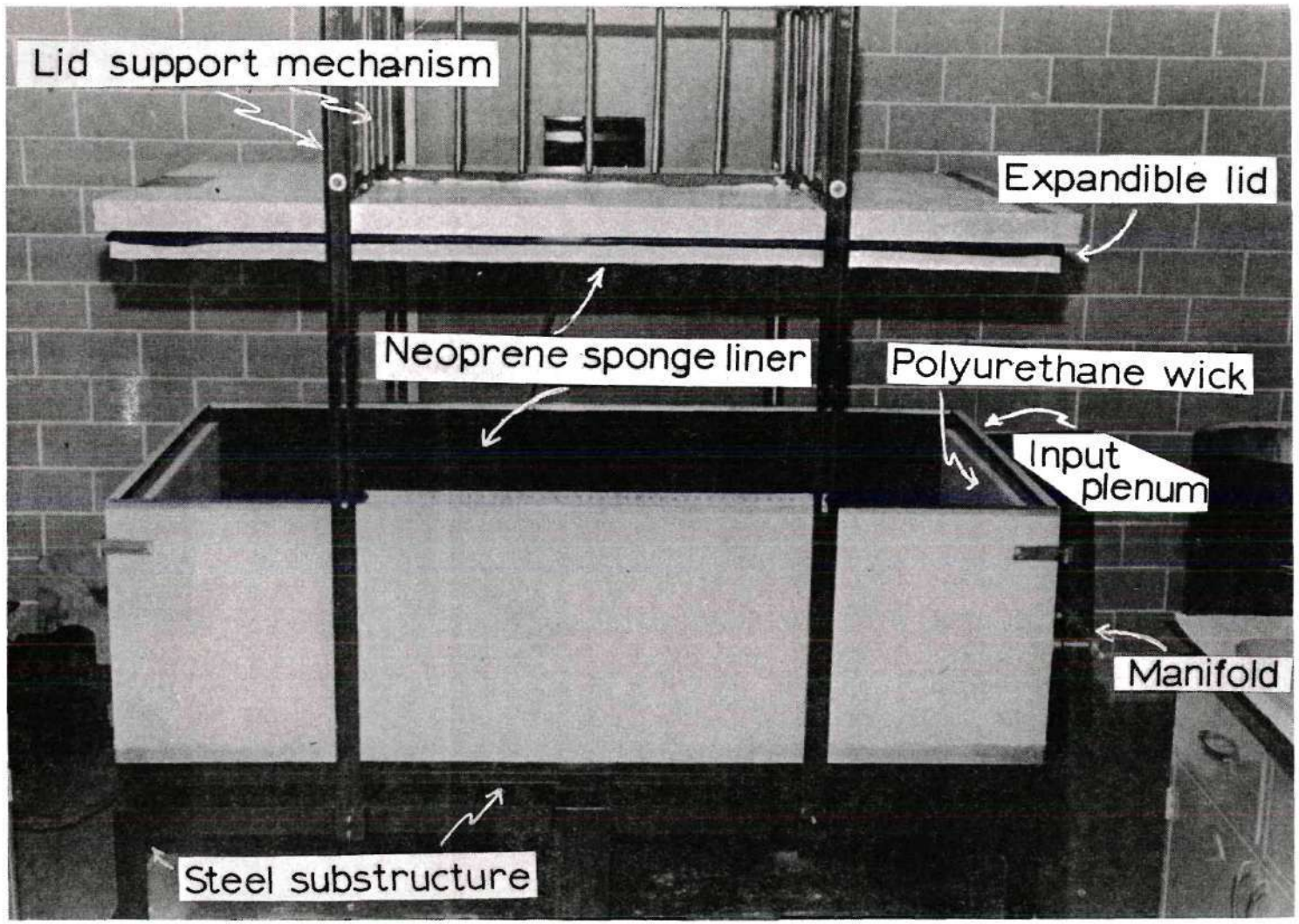


Figure 7. Side View of Sand Bed Container

the box filled with wet sand. Four 2-inch steel channels were used as uprights (secured to the girder system under the box) to provide horizontal support for the framework from which the lid was suspended.

The lid was constructed in two parts which were connected by a neoprene sheet. The latter formed the sides of a pneumatically-sealed chamber. The upper portion of the lid was formed by gluing a piece of the marine plywood to a piece of the chip-board and suspending it by springs from the framework supported by the two-inch channel uprights. This superstructure of steel channel and springs was used to support the weight of the lid when it was raised. The lower lid consisted of a piece of marine plywood glued to the back of an aluminum sheet on which the neoprene foam was mounted. This part of the lid was shaped to fit the interior of the box closely and to rest on top of the sand where it formed a top seal for the sand bed. The double lid was constructed so that a physical load on the sand could be simulated by increasing the pneumatic pressure between the two parts of the lid. In this experiment, however, only the weight of the lid itself was used to compress the sand.

The input manifold was connected by means of tygon plastic tubing to a small adjustable diaphragm pump and a ballast bottle. The latter served to reduce the pressure surges from the pump and as a means by which the radioactivity was loaded into the system. Twenty-liter plastic bottles and a 20-gallon plastic garbage pail were used to store distilled water for the experiment. The effluent from the sand container was led from the outlet manifold through tygon tubing directly to new, polyethylene, gallon milk bottles.

Vibrator Packer

A Syntron Model VH 65-B electrically driven vibrator was mounted on a square of aluminum, one-fourth inch thick, and cut to fit the inside of the box (about 98 cm on a side). A center support strip about 25 cm wide was welded to the upper surface to provide a mounting for the vibrator and to minimize torsional or bending modes of the mounted vibrator. This was used to compact the bed at intervals during loading and after completion of the loading.

Side-Scanning Radioactivity Detector

The radioactivity was tracked on its course through the sand bed by a special device constructed for the purpose. This side-view scanner was built by placing Nuclear Chicago D-33 or D-34 end-window Geiger-Müller tubes horizontally into holes bored in lead bricks to form a vertical array of six detectors. Thus, the tubes were thoroughly shielded against radiation penetration from the sides. The end-windows were sufficiently recessed into the lead bricks so that the cone of sensitivity was restricted to about 20 degrees in front of the window. This permitted simultaneous detection and quantitative evaluation of the radiation from a given vertical profile of the sand bed without serious overlap at 10 cm spacings along the side of the bed. The scanner and a circuit diagram are shown in Figure 8. Note that the electronics, lead bricks, tubes, long-life battery, and controls were mounted together on two skate boards bolted together side by side. The latter were used to provide mobility and a short turning radius for this apparatus in rather crowded conditions.

Six tubes were used in the scanner with the lowest one at the level of the bottom of the bed and each subsequent one separated on a five cm

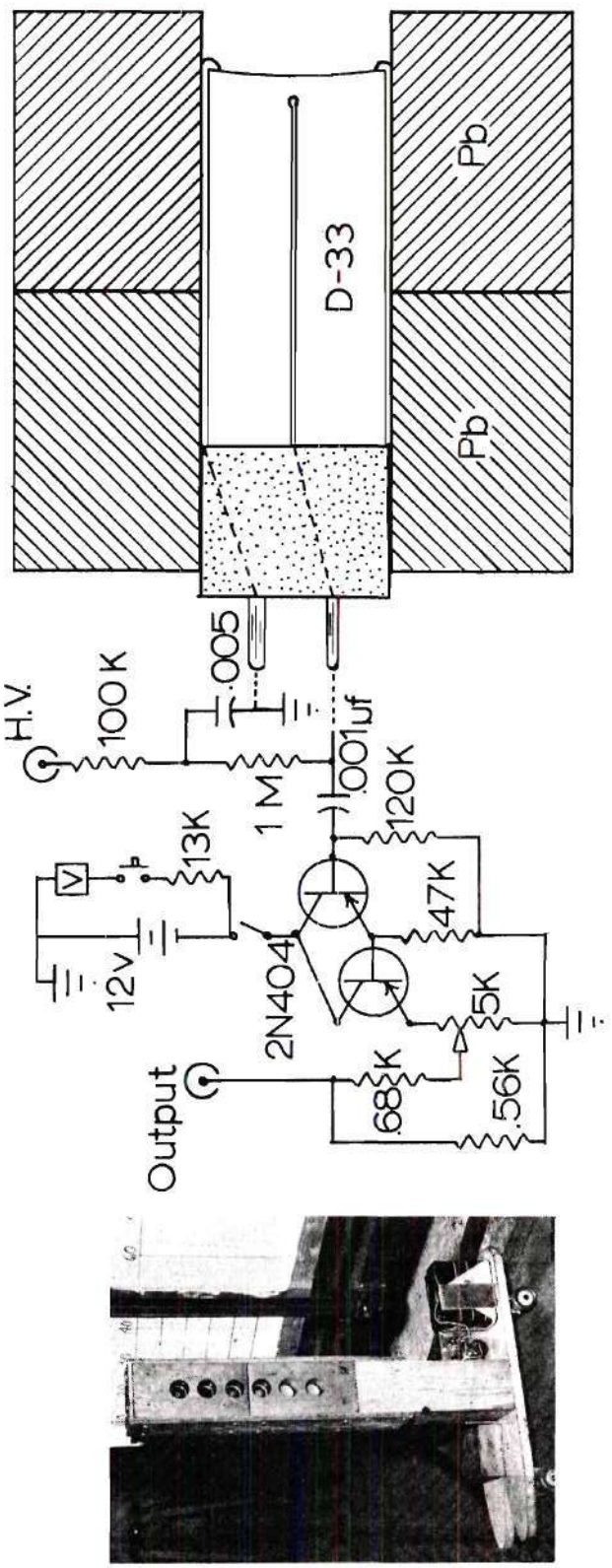


Figure 8. Side-Scanning Geiger Müller Device

center, one above the other, for 25 cm total. Each of the tubes was connected through a transistorized circuit by a common lead to a TMC 400-channel pulse height analyzer. The output of each Geiger tube was taken off a voltage-dividing network so that a different voltage pulse was fed into the analyzer for each detector. By adjusting the output amplitudes of the detectors to differ by fixed amounts, the response of all six tubes could be recorded at once by using this analyzer and printing out the spectrum for a given horizontal position of the scanner.

Flame Spectrophotometer

The alkaline element content of the influent and effluent streams was determined by use of a Coleman Universal Spectrophotometer, Model 14, with the natural gas and oxygen flame attachment, Model 21. Interference filters were used to provide specific analyses for sodium, potassium, and calcium in mixtures of all three. Calibration curves prepared from standard solutions were used to evaluate the results obtained by the flame analyses.

Conductimeter

An overall evaluation of the cation content was made by use of a conductivity meter. Calibration of the meter was accomplished with standard sodium solutions so that the total conductivity could be determined in sodium equivalents as well as in micromhos. The conductimetric readings were taken with a small, portable, transistorized Solubridge, Model RB-3, from Industrial Instruments. The conductimeter was limited to minimum readings of 25 micromhos but it was very useful in the beginning of the experiment and during the time that the radioactivity was being received in the effluent.

Particle Counter

Particle counting was done with a Coulter Counter, Model B. Unfortunately, with the 100-micron diameter orifice available for the experiment, the particles were at or below the lower sensitive range of the unit. Nevertheless, due to the distributive nature of the particles, it was possible to evaluate the relative particulate load in the effluent at any one time by measuring the number of particles of two to three microns mean diameter, even if the entire distribution of sizes could not be measured. Normal saline, filtered through 0.45 μ pass membrane filters, was used as a carrier and diluent for the particles in the apparatus.

Detector for Radioactivity in the Effluent

Detection of radioactivity in the effluent was accomplished by use of a two-inch cylindrical NaI(Tl) scintillation crystal mounted on a Dumont No. 6292 photomultiplier tube. The output of the tube fed through a preamplifier to a TEN decade scaler, Model SA-250, obtained from Nuclear Supplies. A glass Marinelli beaker was employed to contain the sample around the crystal. Lead bricks were piled around the crystal to provide shielding from extraneous radiation while providing easy access to the Marinelli beaker. Sand cores, taken from the sand bed after the water flow was terminated, were placed on top of the crystal in plastic beakers for measurement of the radioactivity they contained.

Filtering Apparatus

Standard glass units acquired from Millipore, Inc. were used for all the filtering studies made in conjunction with the analyses of the effluent samples. Membrane filters, 47 mm in diameter, composed of cellulose esters, were used in the three pore sizes, 0.45, 0.10, and 0.01 microns.

This particular composition permitted ready solution of the membrane in organic solvents so that electron micrographs subsequently could be made of the particulate matter without interference from the membrane.

Devices for Examination of the Particulate Matter

Microscopic examination of the sand grains was made with an American Optical binocular microscope, and sieve analyses over the size range from 25 to 1000 microns were made with a set of stainless steel Tyler screens. By and large the clay particles used were too small to be viewed effectively in the binocular microscope, but examination of the original ore was undertaken to establish the general structure of the sediment from which the clay was obtained.

Further identification of the clay and other particles obtained from the sand bed was made with a Norelco X-ray Diffractometer and with two electron microscopes, an RCA, Model EM U-3, and a Philips, Model EM-200.

Materials

The Sand

A supply of 8000 pounds of sand was obtained from the Pennsylvania Glass Sand Company of Columbia, South Carolina. As it is used for the manufacture of glass, the Company customarily screens, washes, and dries the product before packaging it dry in 100 lb paper bags. The grade chosen for this experiment was small-grained but free of fines.

A dry-sand sieve analysis was made to determine the particle size distribution. Table 4 shows this distribution of sizes by weight as determined by a series of Tyler stainless steel screens on 200 grams of

Table 4. Particle Size Distribution by Weight of the Sand Used in the Experiment

Mesh Size μ	Weight gm	Total Recovered %	Mean Dimension on Screen μ	Smaller Than %
63	0.000	0.00	--	0.000
74	0.374	0.19	89.5	0.007
105	41.180	20.67	177.5	0.195
250	139.086	69.84	375.0	20.865
500	17.138	8.61	603.0	90.705
707	1.366	0.69	854.0	99.315
1000	0.000	0.00	--	100.000

the material. The distribution peaks at 250 microns mesh dimension and drops below significant values at 63 and 1000 microns. Traces of particulate matter below weighable proportions could be detected on the 63, 37, and 25 micron screens as well as on the pan, which collected material smaller than 25 microns. Generally speaking, however, the fine material present in the sand appeared to be closely associated with the larger grains and did not separate in the process of dry screening.

That this sand is a prepared fraction of a more complete size range can be seen in Figure 9. The distribution was peaked mechanically at the mean size by the manufacturing process although this abnormality does not cause any particular divergence from the log-normal distribution.

The grains, of which the sand was composed, were generally equidimensional, subangular to rounded, non-frosted, clear particles of quartz. Some quartzite and muscovite were present also in quantities probably less than two percent of the whole. Despite the individual grain clarity, the bulk sand had a slight buff cast, which was due no doubt to a faint iron stain in crevices on some of the grains. Gross coatings of the sand particles were not obvious, however, when viewed by the low power binocular microscope.

The Clay

A dry-packaged, 100 pound bag of Hydraglos kaolin was obtained from the J. M. Huber Corporation mine and production facility at Wrens, Georgia. The specifications on this clay were that it was 92 percent smaller than two microns with a mean particle diameter of 0.37 μ. Figure 10 shows the particle size distribution by weight of this clay compared to two other clays. As may be seen, the Hydraglos clay is not distributed

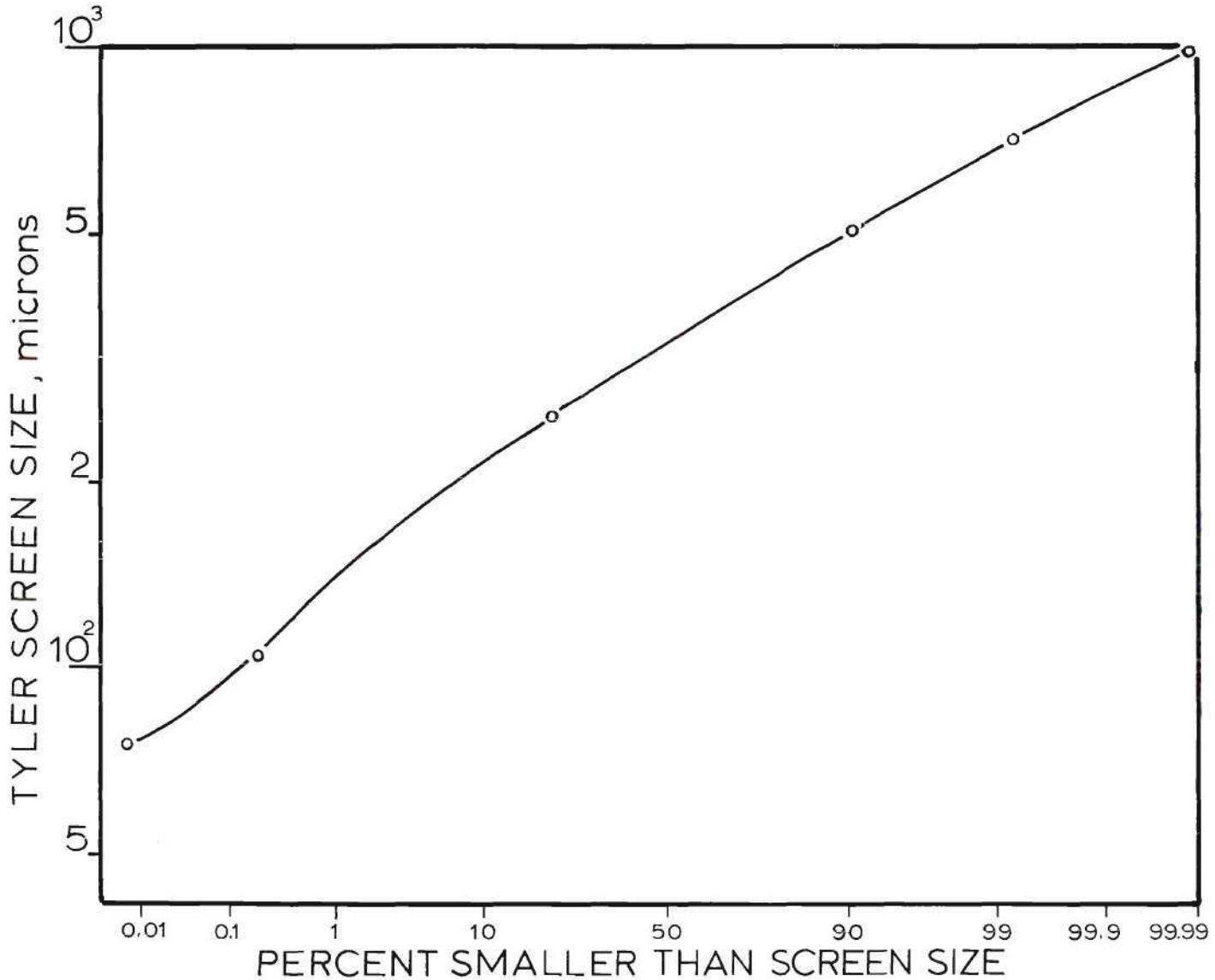


Figure 9. Particle Size Distribution of Pennsylvania Glass Sand

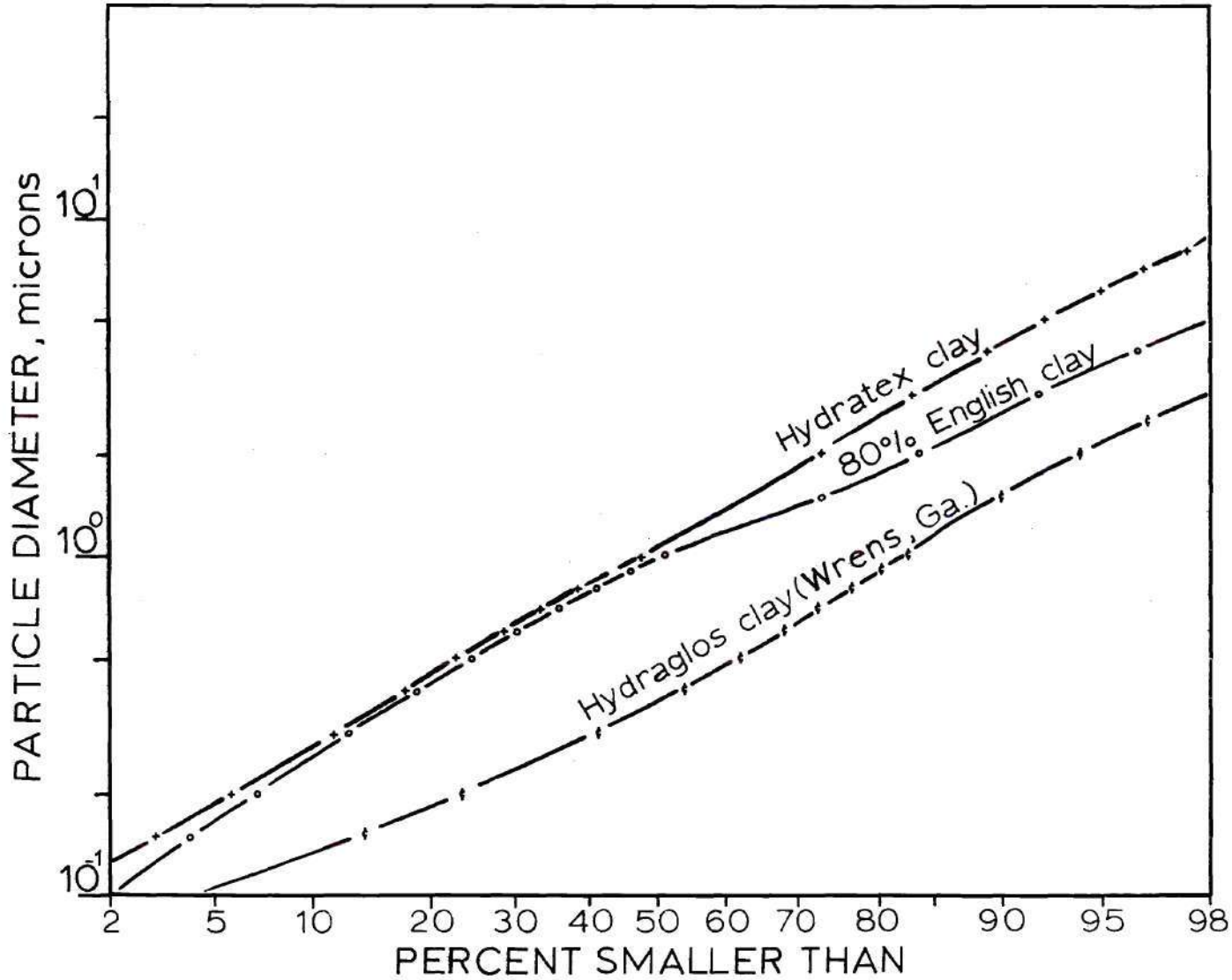


Figure 10. Particle Size Distribution of Kaolin Used as Tracer Carrier Compared to Other Typical Clays

as log-normally as is the Hydratex clay. For the most part, however, the former does not depart greatly from that of a log-normal distribution. The Hydraglos clay had the advantage, for use in this experimental work, that its mean diameter was only one-third that of the coarser Hydratex clay.

Chemicals and Radioactive Materials

The only chemical used in macro-quantities was sodium carbonate to disperse the clay, except for the standard spectrophotometric solutions used in the flame analyses and the normal saline used in the particle counting. The spectrophotometric standards were made up from concentrates supplied by Scientific Products as 250 meq/ℓ sodium, 10 meq/ℓ potassium, and 100 meq/ℓ calcium. These standards were prepared in several dilutions to check points on concentration versus instrument-response curves that had been developed by diluting reagent chemicals. The standards also were employed (sodium only) to obtain a data curve relating conductivity to sodium content. The normal saline was either provided by Harleco in prepackaged, ready-to-use form or it was prepared from reagent sodium chloride (Fisher) and distilled water at 8.5 gm NaCl per liter and filtered through a 0.45 μ Millipore membrane filter.

Sodium Carbonate. Dispersion of 0.5 gm of clay, as used in the experiment, required 3.45 gm of Na_2CO_3 (Baker reagent grade). With the clay initially in nominal sodium form, little cation exchange should have occurred, but the peptizing effect of the carbonate ion adsorption on the platelet edges probably separated the flocs that made up the clay.

Radioscandium. The radioactive chemical used in trace amounts in this experiment was scandium-46. Scandium-46 has several material advantages in an experiment of this type. First, it has a moderately long

half-life (84 days). This permits considerable experimentation over a period of several days without the necessity of allowing for radioactive decay between samples. Yet, it is not so long that is poses a problem from the standpoint of disposal of the waste after the experiment is completed. Second, it has penetrating gamma rays of an energy such that they suffer minimal adsorption in passing through the thickness of sand and the sides of the sand container. The two principal gamma rays have energies of 0.89 and 1.12 MeV. Third, scandium's only common ion is trivalent; it has many of the chemical characteristics of the rare earths so common in radioactive wastes; and it has an ionic radius nearly the same as that of trivalent ruthenium. Fourth, it is an element commonly associated with clay and the lateritic fraction of soils, yet its geochemical distribution in the earth's crust is imperfectly known. Consequently, its interaction between water and soils is of interest by itself.

The isotope was obtained from the Isotopes Development Center, Union Carbide Co., Oak Ridge, Tennessee, as the chloride dissolved in 1.34 N HCl at a specific activity of 68,250 mCi/g. The scandium was supplied in one milliliter of the acid at a concentration of 0.32 mg/ml scandium with a total activity of 21.84 ± 3% mCi on the assay date of 12/8/66. As of 7/17/67, the date of the introduction of the radioactivity to the sand bed, the radioactivity had decayed such that 0.8 ml of the original solution had an activity of 2.64 mCi.

Analytical

It is useful to consider separately the analytical procedures and

the general experimental procedure because, by-and-large, the former are relatively straightforward and conducted in a routine manner throughout the course of the experiment. The analytical procedures that will be considered are the following:

1) Flame spectroanalysis
2) Conductimetry
3) Filtering
4) Particulate Analyses
    a) Coulter Counter
    b) Optical density
    c) X-Ray Diffraction and Electron Microscope
5) Radiation Scintillometry
    a) Effluent
    b) Cores

Flame Spectroanalysis

Aliquots were taken of each gallon of water passed through the sand bed. These were placed in disposable beakers, designed for the purpose of aqueous-solution flame analyses, supplied by Scientific Products (Cat. No. B 2718). Generally, about 30-40 samples would be prepared for analysis for a given element and then evaluated consecutively over a relatively short period of time. Then the apparatus was readjusted and the beakers refilled as needed to analyze for the other elements. Use of interference filters for specific analyses of sodium, calcium, and potassium made it possible to work with no noticeable interference between the elements.

Reproducibility ranged little over the major range of analysis of 10^{-3} to 10^{-4} molar and the systematic error in this range was on the

order of one to two percent. In the lower range of 10^{-5} to 10^{-6} molar, the reproducibility depended on such variables as height of solution in the beaker, oxygen pressure, cleanliness of the atomizer and screen, etc. By keeping the beaker full, the oxygen standardized at 13.5 psig, the natural gas at full line pressure, and the atomizing assembly clean (using an ultrasonic bath), the reproducibility in the lower range was kept within about five percent deviation. Although somewhat better data reproducibility was noted for sodium than for potassium or calcium at the same level of concentrations, this level of systematic error was taken as satisfactory, since the relative values of the data were of prime importance in this part of the experiment.

In the actual operation of the flame spectrometer, the galvanometer used to measure the energy received from the photocell by a Wheatstone Bridge arrangement was zeroed on its scale with a blank of distilled water for each decimal-molar range employed. A series of standard solutions of 0.1, 0.01, 0.001, etc. molar were used to set the 100 percent value for each range. Samples then were tested with an occasional check against the blank and standard to compensate for any scale shifting. Deliberate comparison could be made of the results by running large numbers of samples at the same time without recourse to the absolute values of the measurements as long as the calibration remained steady.

Conductimetry

About 200 ml of each gallon of effluent was placed in a disposable polystyrene specimen container (Scientific Products Cat. No. B 7935) and the conductimeter probe was placed in the water so that the electrodes were submerged. The probe was then raised and lowered several times to

remove the air from around the electrodes, and a conductivity measurement was taken with the Solubridge apparatus. Its sensitivity was greatest in the 10^{-3} to 10^{-4} molar range and the deviation of the data was probably on the order of one to two percent. Conversion of the conductivity data to sodium equivalents made direct comparison to the flame analyses possible.

Filtering

A 500 ml glass Millipore filter funnel was fitted to a 47 mm, sintered glass, membrane holder on which a membrane was placed and this assembly was arranged on a one liter vacuum flask. Vacuum was obtained by use of a Gelman air pump. For small quantities of liquid, the sample was pipetted directly onto the membrane filter with the flask under vacuum. With large volumes, the funnel was kept about three-fourths full until the filtration was nearly complete, then it was allowed to drain through. The funnel, membrane holder, and flask were cleaned between filterings with Alconox detergent and rinsed with distilled water. The 0.45 μ membrane (HAWP-047-00) was used to prepare some of the normal saline solution used in the Coulter Counter, and a 0.1 μ membrane filter (VCWP-047-00, Millipore) was used to trap particulate matter from the effluent for electron microscope and x-ray diffraction studies.

Particulate Analyses

Particle Counting. The Coulter Counter used had an orifice of 100 microns or about the same mean hydraulic radius (25 μ) as that determined for the sand bed (19 μ). The sample suspension was prepared by taking a 10 ml aliquot from a given gallon of effluent and mixing it with 90 ml of normal saline solution. Timed determinations on such mixtures showed little change in particle count over a period of 20 to 30 minutes. The

experimental determinations took only five to ten minutes, which was not sufficiently long for the change in ionic strength of the suspension to alter the particulate distribution materially. A similar determination made on the normal saline solution by itself or with 10 ml of distilled water added to 90 ml of the normal saline solution was used as a blank. This made possible a reasonable determination of two, three, four, and five micron sizes. However, measurements of particles smaller than 1.5 microns were subject to deviations which were dependent on the number of larger particles, electronic blocking, etc. It was not advantageous to use a smaller orifice, because that would have required prefiltration of all the samples to prevent plugging of the orifice by extraneous silt-size particles.

A few spot checks on the sand bed effluent showed no statistically pertinent counts of particles larger than six microns. Each count represented the passage of a particle through the orifice at the dilution employed. The upper and lower discriminators were set so that any given size, say three microns, would be a nominal mean of sizes lying between 2.9-3.1 μ particles. Calibration of the range was accomplished by use of latex particles supplied by the Dow Chemical Company and some fine-grained Biorex ion-exchange resin. The former had a peak in particulate-size distribution slightly larger than one micron; the latter had a peak at about five microns. Neither peak was very sharp, but it was possible to verify the range by electronic settings using these standard particles. Here again, since only relative values within a given calibration were important for this experiment, the absolute values were not particularly pertinent. The deviation appeared to be about 0.2 μ at the lower end of

the range at most, and this may have been caused by incomplete dispersion of the latex, causing a shift in the position of the broad peak on the size range.

Optical Density. Inasmuch as the Coulter Counter was limited in its ability to sense the presence of particulate matter smaller than one micron, a second means of analysis was the use of the Coleman Universal Spectrophotometer, described above in association with the flame photometer, to determine the optical density of the effluent samples. This proved to be a useful way to get an overall evaluation of the relative quantity of suspended particles regardless of their size, since the samples were all colorless or at most tinged slightly yellow. The scale range was set by using the first gallon of effluent as the maximum particulate load to be expected. The controls were adjusted for a maximum reading for this sample using light of 460 millimicron wavelength. Distilled water served as the blank or zero setting on the scale. Standard Coleman one-cm square cuvettes were used for this purpose.

X-ray Diffraction and Electron Microscopy. The particulate matter caught on the filter membrane was transferred to a glass slide by mounting a wide strip of the membrane on the slide with plastic tape and subjecting it to Copper Kα radiation using a nickel filter for beta shielding with a Norelco X-ray Diffractometer. A time constant of two seconds and a high voltage of 40 kV at 25 milliamps were used for operation of the x-ray tube. The scale factor was 2×10^2 with one degree (2θ)/min scanning rate and pulse height analysis at 90 percent.

The filter membrane and particulate matter were then removed from the glass slide. Two alternate techniques followed for preparing electron

microscope samples. One used carbon coating of the surface and subsequent solution of the membrane by acetone for preparing the pure kaolin. The other used shadowing with platinum at a 3:1 shadow angle, carbon coating of the upper surface, solution of the membrane as before, and then dissolution of all siliceous materials with HF. This latter action was taken to establish the existence if any, of particles that were not composed of siliceous mineral matter. Both the fine particulate matter from the bed found in the leachate and the particulate mixture in the radioactive effluent were examined in this manner. The prepared membranes were then placed in the electron microscope for examination and photographic recording.

Radiation Scintillometry

Effluent. The effluent radioactivity was analyzed by placing 150 ml of sample in a glass Marinelli beaker and placing it on a NaI(Tl) crystal as described in the section Apparatus. Background determinations were made with distilled water substituted for the sample in the beaker. Relatively low backgrounds were obtained by shielding the crystal and using a transistorized decade scaler. Sufficient counts were obtained from the effluent while the radioactivity was being discharged from the sand bed to limit the counting time to one minute per sample. Several samples and blanks counted for ten-minute intervals were analyzed, while looking for traces of radioactivity coming through early, to check the one minute background determinations.

Cleaning procedures on the Marinelli beaker varied from simple rinsing with distilled water to scrubbing out with Alconox detergent and subsequent rinsing with distilled water or, in the extreme, to rinsing

with a 1:1:2 mixture of HF:HCl:H_2O. The latter was used only when other means of cleaning failed to reduce the count of the beaker to the general background level when filled with non-radioactive water. This was neccessary only twice when some radioactivity had been left in the beaker overnight. It was a very effective means of activity removal.

Cores. The cores taken from the bed were analyzed with the same counting apparatus as that used for the effluent radioactivity. The core was placed in the type of cup used for the conductivity measurements, broken up and stirred together to make the radioactive mixture homogeneous, and packed with a plastic rod into the bottom of the cup. The sand packs in the cups averaged about one-half inch thick with a diameter about the same as the top of the crystal, permitting reproducible geometry. For the determination of the radioactivity, the cup was simply centered on top of the crystal and counted for one minute. Since each sample had its own cup, it was not necessary to clean out the container between analyses. With this constant geometry, it was possible to obtain data on the relative distribution of radioactivity in the sand bed without recourse to absolute values.

Experimental Details

Preparation of the Sand Bed

Cleaning. Since the sand bed had been used previously, it was necessary to clean it up as much as possible to remove the residue of other experiments. First, the entire sand pack was removed from the container and the latter vacuumed out to remove all loose sand particles. Then the wick material was removed and discarded. The end doors were

removed and cleaned with vacuum and air blast to remove the sand that had penetrated during the removal of the previous bed. Next, the doors were replaced and new wick material was placed on them and cemented in place with rubber cement. The neoprene-covered interior surface of the box was scrubbed with a brush and distilled water and wiped with a five percent solution of hydrogen peroxide for bacteriostasis. Finally, all the neoprene was given a final rinse with distilled water and the rinse water removed through the two drain ports in the bottom of the bed.

Sealing. After the rinsing of the box, the end doors were sealed in place with General Electric Silicone Construction Sealant (SE-1201). Since this material sets by adsorbing water from the air, two hours spent in drying the box interior with a fan provided a dry box and sealed the doors at the same time. Once the caulking compound had set, the box was filled to a depth of 15 cm with distilled water to check for leaks before loading with sand. The leaks detected were marked, the water drained, the leaks plugged, and the box rechecked for leakage. Finally, all the water was drained from the bed and the interior surfaces were thoroughly air-dried overnight before the packing was begun.

Packing. The actual packing process involved simply physical labor. The dry sand was brought in by wheelbarrow and float in the 100 pound sacks. The drain ports at the bottom of the bed were covered by a thin layer of the polyurethane wick material, cemented in place. This covering permitted draining the sand bed of any excess water (above the capillary demands) later without permitting the sand to penetrate the pipes below. With the drains covered, one of the sacks was opened and the contents dumped into the bed and spread evenly over the bottom, obtaining as level a layer as possible. The vibrator packer was placed on

the sand at one end of the box and allowed to pack for five to ten minutes while more sand was being added at the other end. By cyclically adding and packing, the desired total thickness was obtained.

After the bed had been thoroughly packed and the upper surface made level as a table top, the lid was forced down to the top of the box and its expandable section allowed to lower onto the top of the sand. With the top surface of the sand flat and level, the neoprene sponge covering the underside of the lid made a close fitting seal to the sand. The clearance between the lid and the sides of the box was about one-sixteenth of an inch. The ends of the lid compressed the upper portion of the end-door wicks producing a reasonably good seal there also.

Filling. A large supply of distilled water was needed for this experiment. It was prepared by allowing a still to fill several 20 liter polyethylene bottles and a 20 gallon polyethylene garbage can. Water was siphoned from these containers to the pump and the ballast bottle described in the Apparatus section through tygon plastic tubing. Flow was controlled by finger clamps on the plastic tubing leading from the distilled water containers to the pump and on the tubing leading from the pump to the sand bed input manifold.

Once the bed was packed with sand and ready to fill, flow was initiated by turning on the pump. The flow rate was adjusted alternately with the finger clamps and the rate control on the pump until the water level began to show on a glass-tube level gauge mounted in the center. Then the pump rate was trimmed back to maintain the level about three to five cm from the bottom of the bed. After the wick became wet, the sand imbibed water rapidly and little change was necessary in the pumping rate.

Once the bed filled, the excess water drained through the outlet wick into the outlet manifold and was caught in the first sample collection bottle.

Since the flow rate into the bed was less than one gallon per hour, filling took many hours. Consequently, the flow was allowed to stop at night. While causing no particular problem, these resting periods did cause changes which appeared as fluctuations in the analytical data taken on the effluent.

Leaching. Once the sand pack had filled with water, pumping was continued with each gallon of effluent collected in a different plastic bottle for analysis. Conductimetry, flame analyses, and particle counting were done as soon after sample collection as possible, usually within a few hours. By keeping track of the conductivity and potassium concentration in the effluent, a somewhat arbitrary point was determined at which the radioactivity could be added to the influent. This point was established when the conductivity of the effluent water dropped below 25 μmho and the potassium concentration reached what appeared to be a plateau. The radioactivity was introduced during the collection of the 31st gallon of effluent or after about three-fourths of one bed-volume of distilled water had been introduced to the bed.

Introduction of the Radioactive Influent

Preparation. In order to ensure the uniform distribution of the radioisotope on the particulate matter, an effort to disperse the clay and the radioisotope was made before they were mixed. The 0.5 gm of clay was weighed and placed in a blender with 3.5 gm of sodium carbonate as a dispersing agent in about one liter of water. The mixture was blended at low speed for about 15 minutes, filtered through a Millipore back-up pad to remove lint and other extraneous particles of relatively large size,

placed in a plastic gallon bottle with 1800 ml of distilled water, shaken thoroughly, and allowed to stand for one hour. In the meantime, the radioactive tracer solution was measured with a pipette and diluted with 800 ml of water. This too was set aside for the remainder of the hour. At the end of this time, the bottle containing the clay was placed on a magnetic stirrer and a Teflon-covered stirring bar placed in the center of the bottom of the bottle. Stirring was adjusted so as to be non-turbulent. The radioactive water was added slowly to this swirling suspension. An additional 40 ml of distilled water was used to wash out the bottle that had contained the radioactivity.

This mixture, 0.5 g clay (kaolin), 3.5 g Na_2CO_3, 2.64 mCi Sc^{46}, 256 μg of stable scandium (Sc^{45}), and 51 mg of HCl in 3640 ml of distilled water, made up the radioactive suspension. The final radioactivity of this initial influent to the sand bed was 0.773 microcurie per milliliter. A 350 ml portion of this suspension was taken aside as a standard on which analyses such as filtering, cation determination, and radioactive analyses, could be performed.

Injection. With the pump stopped, the radioactive mixture was placed in the ballast bottle and allowed to drain for a period of 30 minutes into the plenum chamber of the input door. The pump was then started and fresh distilled water was pumped into the ballast bottle to rinse it. The pump was again stopped and the bottle allowed to drain. After draining the bottle, the pump was started again at the rate desired, and the principal part of the experiment was begun. Continuous pumping at a rate adjusted to one ml/sec was maintained as closely as possible during the collection of the next 266.4 liters and samples were taken every 3.6

liters (roughly every gallon) for cation, particulate, and radioactivity analyses.

Following the Radioactive Tracer

Radiation Field. Since a relatively large radiation field was involved initially (about two mr/hr at six feet), the area around the sand bed was cordoned-off and a radiation warning sign posted. Surveys with a portable Geiger counter showed the radioactivity had spread throughout the plenum chamber. It did appear to be slightly more concentrated at one end of the door than the other, but the difference was relatively small. Initiation of the pump supplying distilled water to the door, however, caused most of the radioactivity to move into the sand. Shortly thereafter the external radiation field dropped to 2 mr at six inches from the input door.

Side-Scanning. The side scanner was positioned with the end windows of the tubes about one inch away from the side of the sand bed. Starting at the edge of the container with readings at every 10 cm along the side of the bed, data were taken as long as the counts remained above the background. The count obtained with the scanner located at the end of the bed away from the radioactivity was used as nominal room background. Background readings taken in another room behind a heavy concrete wall away from any radioactive sources verified that the counts taken at the end of the bed were valid background readings.

With the six tubes all feeding information at one time to the 400-channel analyzer and using automatic printout and reset, it was possible to scan the whole section of the bed containing radioactivity in about 15 to 20 minutes per side with little difficulty. With a displacement rate of the activity in the bed of about five cm per hour, these readings were

essentially "instantaneous" views of the relative location of the radioactivity at any given time. The surveys of the sides were made at 30 minute intervals for the first few hours, then every three hours for the remainder of the day and night. The final scans made two or three days later were at six to twelve hour intervals.

Differentiation. Within about six hours it became possible to distinguish between the activity being held by the bed and that remaining mobile. Subsequently, only that section of the bed which contained the mobile activity was emphasized by scanning from the side and only an occasional scan of the whole bed was made. The side-scanning was discontinued after the mobile radioactivity peak had passed from the sand bed. The period over which side scanning was actively pursued lasted about 60 hours.

CHAPTER IV

RESULTS

Due to the fact that many of the analytical results are pertinent to one another, it is useful to describe the results of the many analyses first and then to discuss them more fully.

The Analyses of the Leachate

Cation Content

Figure 11 shows the sodium, potassium, and calcium concentrations in the portion of the effluent which passed from the sand bed prior to the breakthrough of the radioactive suspension. Since only distilled water was passed into the bed ahead of the radioactivity, the contents of this portion of the effluent were derived solely by "leaching" the sand; therefore, it is henceforth referred to as the leachate. The total cation content as determined by the conductimeter is shown in the figure as a solid black line that begins at the left margin and extends through sample 37. The conductivity is plotted in terms of equivalent sodium content so that the data could be directly compared to the cation analyses.

The trends revealed by the cation data are indicated by straight lines. These lines actually represent a true exponential function about which the real data fluctuated. These fluctuations in large part were caused by the time schedule followed in pumping water into the bed. On the figure, points are noted indicating overnight pauses in the leaching of the bed. Following each one is a small peak in the conductivity and

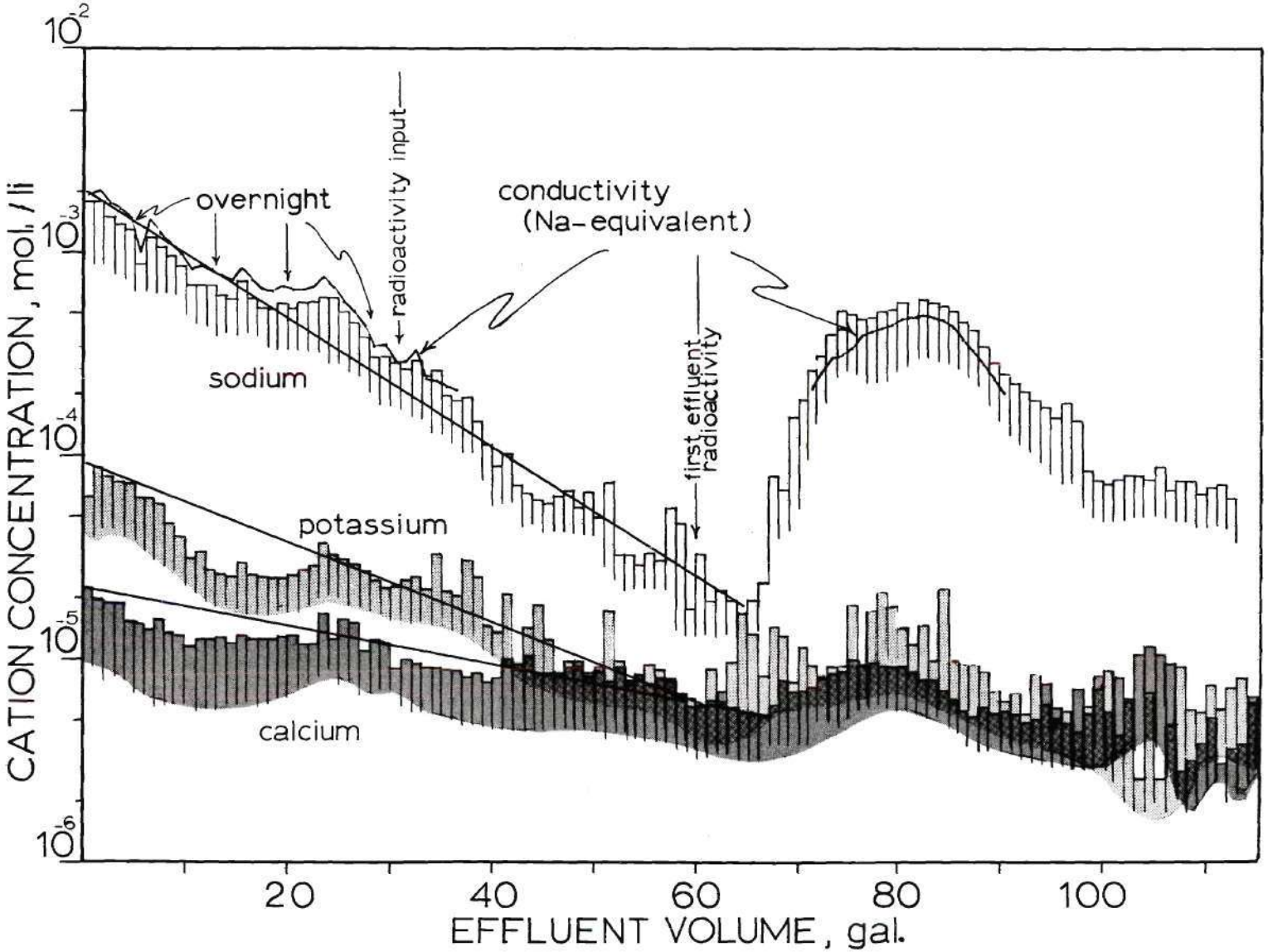


Figure 11. Cation Distribution in the Effluent

some general peaking in the individual cation concentration as determined by flame analysis. The repetitive appearance of the peaks following the overnight breaks within the next one to two gallons suggests that this behavior had its origin in some action taking place in the outlet door.

Other variations in the data may have been caused by the filling schedule. No notes were taken on this point; however, much of the cation data does show a somewhat repetitive cycle involving eight to ten samples which would correspond to a work day with a rate of water transfer of about one gallon per hour.

In the first 60 samples of effluent collected, there were a total of 97.5 millimoles of sodium, 6.4 millimoles of potassium, and 2.4 millimoles of calcium. Taken as residual salts in the sand, these quantities represent 14.3 ppm Na, 1.6 ppm K, and 0.6 ppm Ca, if spread equally throughout a water-saturated void volume of the bed. The initial effluent samples had concentrations of about two millimolar Na with 0.1 millimolar K, and 0.02 millimolar Ca. From these high initial values, the concentration of cations in the effluent followed a general exponential, decreasing trend. The sodium concentration in the effluent decreased far more rapidly than did the potassium or calcium. Of the three ions, calcium was the one which maintained its concentration best in the effluent.

The conductivity data taken over the first 37 samples were effectively the arithmetic sum of the individual cation flame analyses. Apparently these analyses by conductimeter were effectively representing the total, readily mobile cation content of the effluent waters.

Particulate Content

A somewhat similar set of data to that of the cations is that of

the particulate matter measured over the same interval. Figure 12 shows the results of the two micron (± 0.1 μ) particle counting with the Coulter Counter. There are some obvious correlations with variations in the cation analyses. The particulate data, like the cation data, followed a general exponential decreasing trend, but they had a slope which appeared to be intermediate between that for sodium and that for potassium. Similar trends were found for other particle sizes measured.

The total displaced volume between the time of introduction of the radioactivity and breakthrough of the radioactive suspension was about 35 gallons (#31-66). This corresponds quite well to the anticipated pore volume of the bed of 41.5 - 4.8 = 36.7 gallons as derived above. Since the introduction of the radioactivity took place over a period of time and dilution and dispersion occurred in the inlet door and wick before entry into the bed, this early indication of breakthrough is probably the "toe" of the curve and a more proper point of determination might be more desirable. If this is taken to be one-tenth the maximum pulse concentration received in the effluent, the volume displaced that would correspond to that concentration was 68-31 = 37 gallons, or very close to the predicted saturation volume.

The Analyses of the Radioactive Effluent

The portion of the effluent that contained the radioactivity can be considered separately. The cation content and conductivity equivalent are shown to the right in Figure 11. In this section, the conductivity no longer is greater than the total sodium content. In the interval from sample no. 72 to sample no. 91, the sodium collected in the effluent was 33 millimoles. The difference between that and the conductivity equivalent

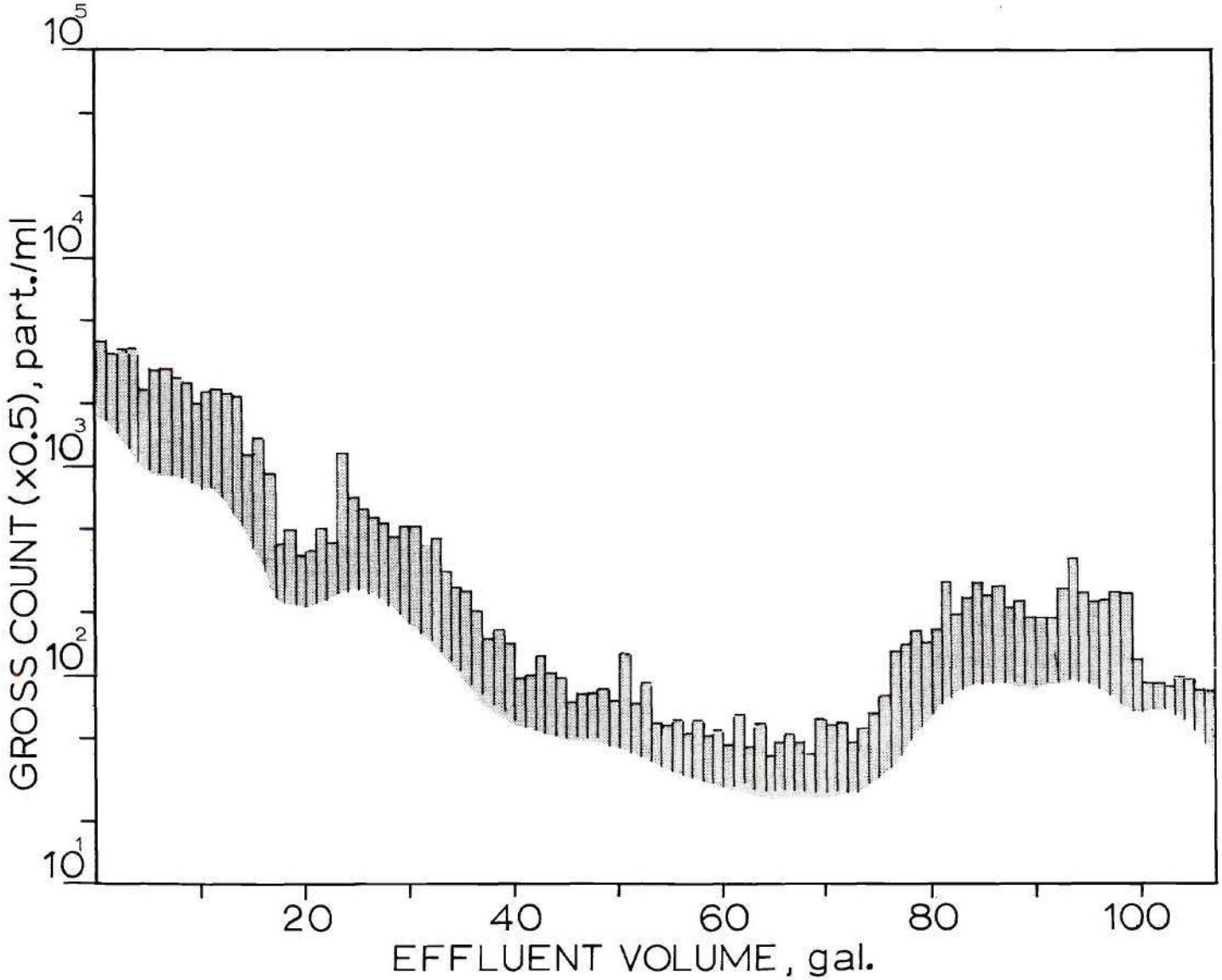


Figure 12. Particle Distribution in the Effluent

was 6.7 millimoles or about one-fifth of the total. The original sodium added to the clay suspension as a dispersant was 65.5 millimoles. Hence, the amount recovered in this portion of the effluent was approximately 50 percent of that put into the bed.

Figure 13 illustrates the results of three determinations, sodium (Na), radioscandium (Sc^{46}), and particulate content (by optical density (O.D.)) with the data curves juxtaposed so that the slopes of the curves may be compared. While it appears that the positive slope on the three curves is nearly the same, comparison of equivalent points (e.g., 0.1 peak maximum) on those slopes shows that the sodium preceded the particulate matter into the effluent by about one-half gallon and that both led the radioactivity by two to three gallons. Actually, a large part of this difference may be only apparent and might disappear on complete normalization of the three curves.

It is also possible that the concentrations of the three are not quite linearly associated, particularly if the sodium is primarily in solution and the scandium is adsorbed to particulate matter. Any shift in size distribution caused by selective retardation of larger particulate sizes by the packed sand grains would lead to corresponding shifts in the relative arrival time of the radioactivity to that of sodium in solution. That selective retardation may be the case is illustrated in Figure 14 presenting Coulter Counter determinations for three size ranges: 1, 1.5, and 2 micron particulate diameter.

If representative points on the upper portion of the positive slope of each curve in Figures 13 and 14 are determined (e.g., 1/e peak maximum), the relative arrival time of each of the quantities can be compared. This comparison is especially pertinent since both the optical density and scan-

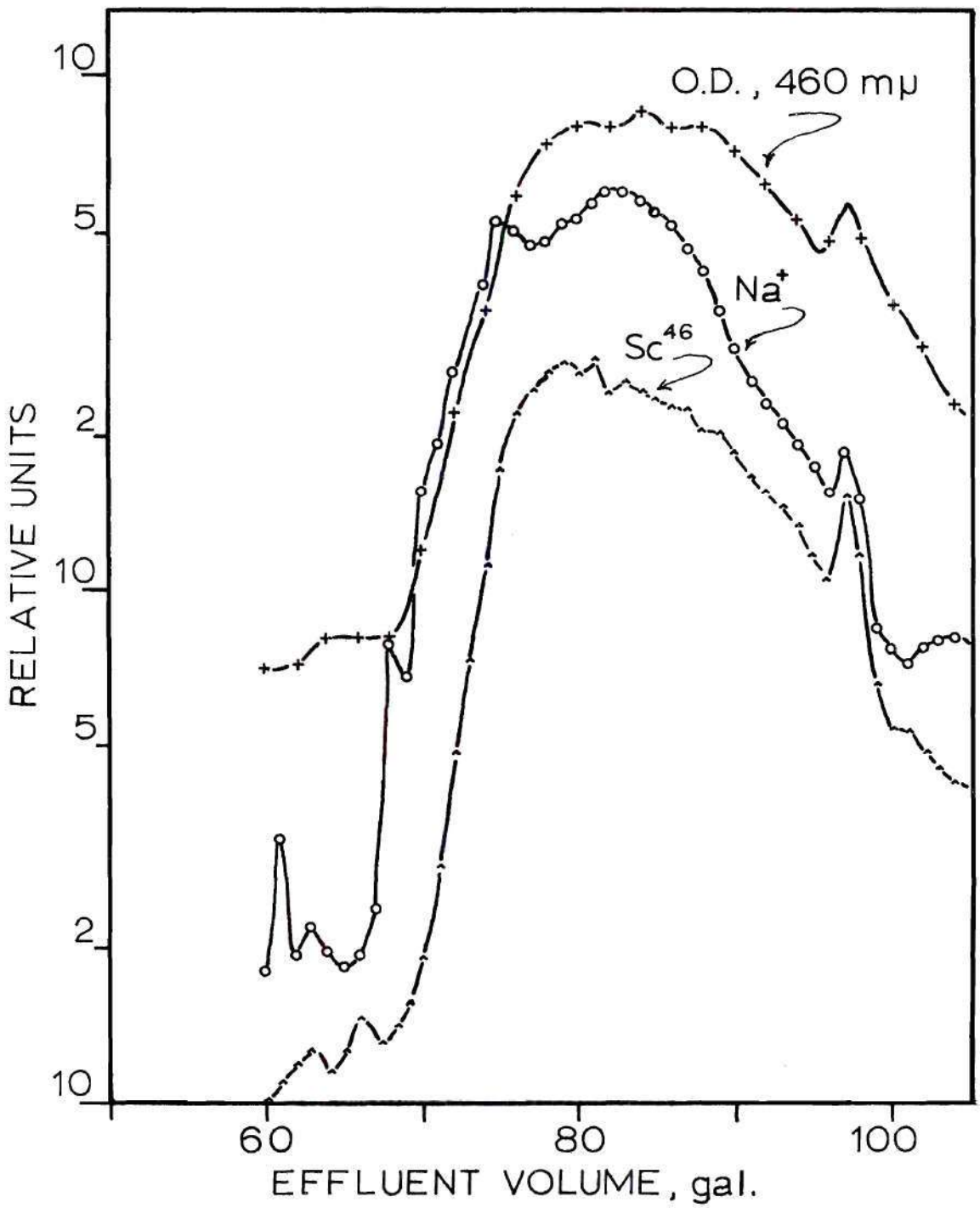


Figure 13. Comparison of Arrival Times and Magnitudes of Radioactive Particulate and Soluble Materials in the Effluent

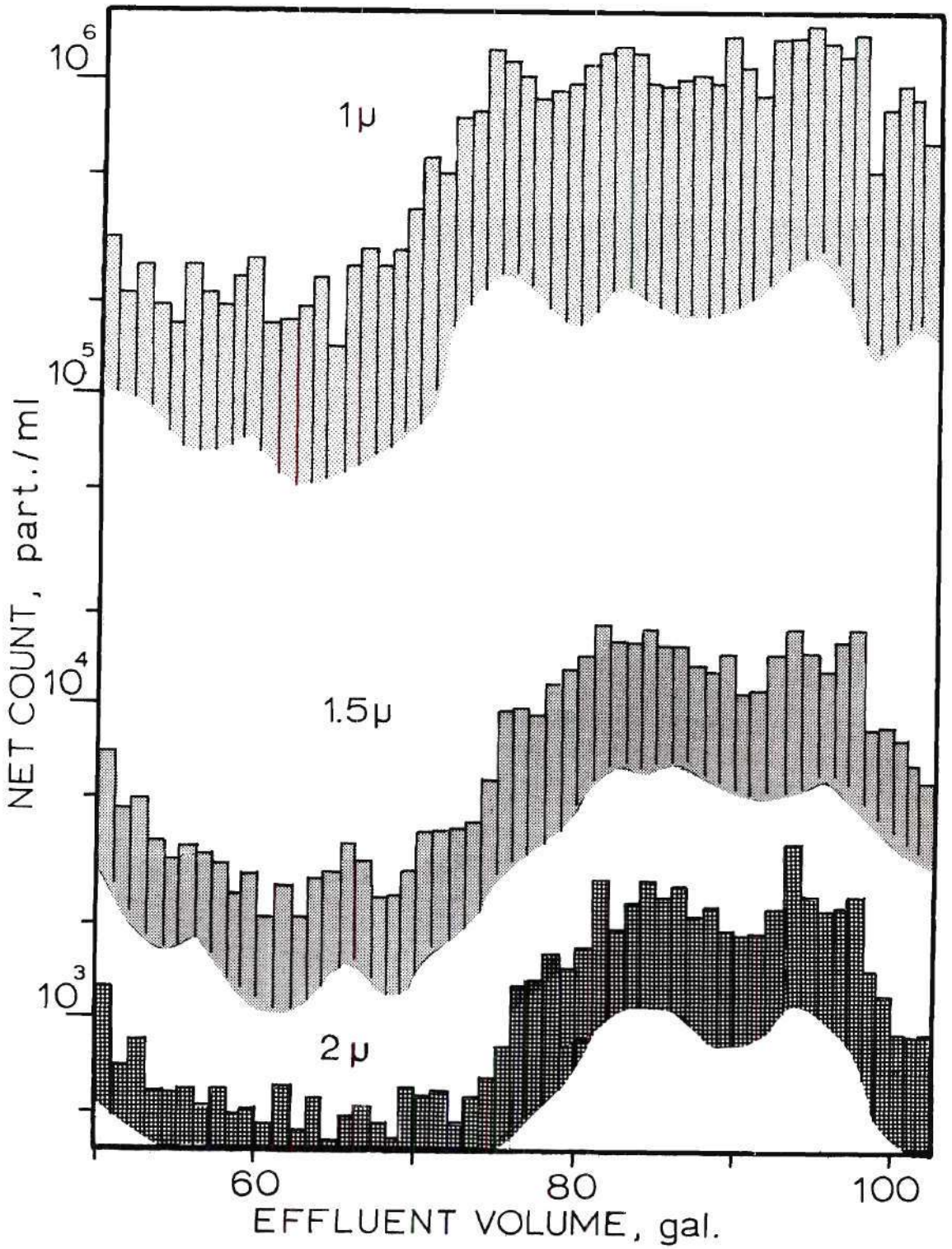


Figure 14. Comparison of the Arrival Times of Selected Particle-Size Ranges

dium content of the effluent are associated in some way with the particulate distribution. These representative points were located at sample 72 for sodium, 74 for optical density, 74 for scandium-46, 70 for one micron, 76 for 1.5 micron, and 77 for two micron particles. While the representative points for the three particulate ranges vary from effluent samples 70 to 77, the average of these points is also the same as that for the optical density and radioactive scandium content, or sample 74. That little or no radioactivity was leached from the particles in passing through the bed is evidenced by the fact that both the radioactive scandium and particulate content are represented by the same effluent sample and both are preceded by the dissolved sodium.

The results are certainly limited in regard to the distribution of the relative particle sizes. However, it was noted qualitatively that the finer particles arrived earlier than the larger particles. This was obvious not only from the position of the representative point described above but also from the general slope and relative position of the first portion of the peak. This is verified by the latter part of the experiment, i.e., around sample 95. In that case, a simultaneous response was recorded for all six determinations shown in Figures 13 and 14, even though the response appeared in different form for each one.

Taking the trend of the last eight samples as a guide for an exponential decrease in activity with effluent sample number, a projection to background counting levels was made to obtain an estimate of the total probable radioactivity recoverable in a reasonable number of samples. This came to 63,662 cpm gross count in 84 samples. Using an average background of 107 cpm per sample, the net total received in the effluent was 54,674 cpm. The input suspension count per milliliter was 67,168 cpm or

22.098×10^7 cpm in 3290 ml. By comparison, the amount of that radioactivity recovered in the effluent after passage through two meters of sand bed represented $54,674/22.098 \times 10^7$ or 2.47×10^{-2} percent of the original input.

The Determination of the Retained Radioactivity

The Geiger-Müller surveys of the side of the sand container gave a relatively continuous picture of the distribution of the radioactivity in the sand. A final survey of the distribution of the radioactivity in the sand was made when the effluent radioactivity peak had passed from the container and the radioactivity of the sides near the effluent end of the box had dropped nearly to original background levels. Typical results from this survey are shown in Figure 15. The terms starboard and port refer, respectively, to the right and left sides of the box facing in the direction of the water flow through the sand. The results are shown in terms of net count received uncorrected for geometry, efficiency, or decay time from the isotope assay date. Since these factors are all constant for the determinations shown, it was not felt necessary to account for them, in this case, where relative values at a given time are more important.

Lines "a" and "b" represent exponential functions that are tangent to the general trend of the first and last portions of the determinations of the data. Correlations between these lines and the data can be seen for both the starboard and port sides. The similarity of this type of construction to that of the graphical solution of a complex radioactive decay curve suggested that a similar solution might be possible in this case. This appeared especially true for the starboard side where the data were under better statistical control than for the port side.

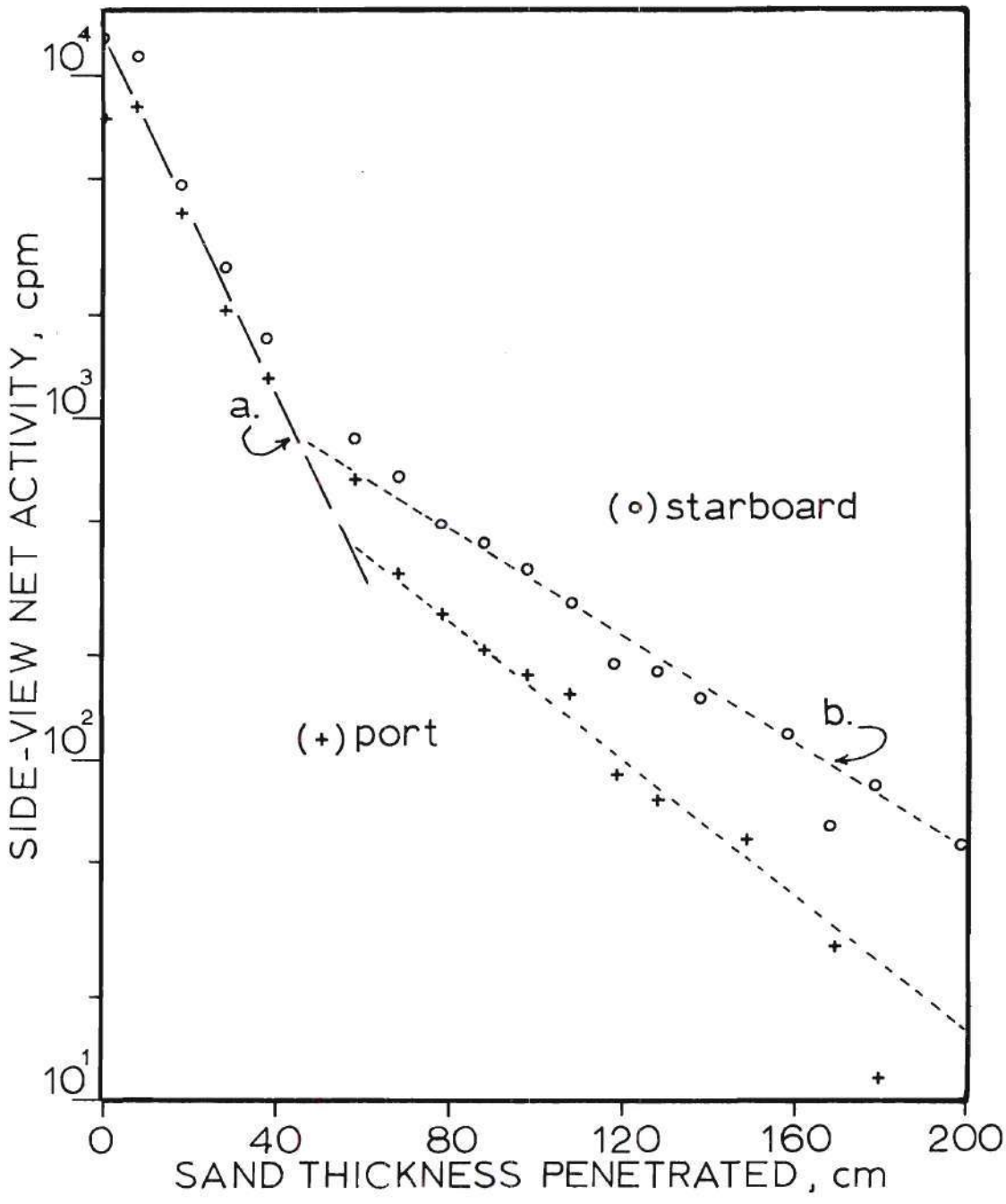


Figure 15. Radioactivity Retained by the Sand Bed Determined by Side-Scanning

Using the Hall-O'Melia approximation for exponential particle removal from waters traversing a sand bed, it is possible to estimate the penetration of two fairly distinct particle sizes. In this, the larger particle was represented approximately by line "a" and the smaller by "b". If it is assumed that "b" represents a log-normally distributed, particulate mass being strained from the water little by little by the sand, then "a" represents a group of larger particles sufficiently well defined to give a fairly distinct distribution in the sand bed. The most likely particles to be making up this group would be micro-flocs of two or three of the particles making up the "b" group. These would behave as a separately defined, statistically large number of particles. Using equations 7 and 8, the particle sizes determined in this way would be about 3.7 microns for the "a" curve corrected for the "b" contribution, and 1.5 microns for the "b" curve.

It was of interest to compare the radioactivity distribution, obtained by side-scanning, with that determined by radioactive analysis of cores taken from the sand bed after the flow was stopped and the excess water drained from the sand container. Table 5 shows the data taken on the distribution of radioactivity at three different vertical levels. The 15 cm depth data compare most closely to the general location of the data illustrated in Figure 15. As a direct comparison, the results from the analyses of the cores cut along the median line of that level are presented in Figure 16. The general shape of the distribution curve is similar to those obtained from the side-scanning. Both curves show a decrease in activity of about two orders of magnitude over the total length of the sand bed.

Table 5. Radioanalyses of Sand Bed Cores

Distance from Input Wick, cm		Distance from Port Side, cm					
	5 cm Height	10	20	30	50	70	90
4		4242*	4209	4051	2320	5770	2197
10		2179	--	1959	2583	2368	3093
20				891	1480	1449	
40					931		
70					259		
110		145			151		137
160					38		
190		36			14		70
	10 cm Height						
4		2171	1776	2578	1794	1818	3170
10		2146	--	1311	1174	1086	2193
20				797	667	639	
40					553		
70					206		
110		41			52		93
160					51		
190		56			10		39
	15 cm Height						
4		1487	1508	2159	4457	1216	2298
10		1025	--	1353	1395	1143	1518
20				805	748	623	
40					536		
70					148		
110		79			71		39
160					52		
190		38			40		39

*All data are in net counts per minute per core.

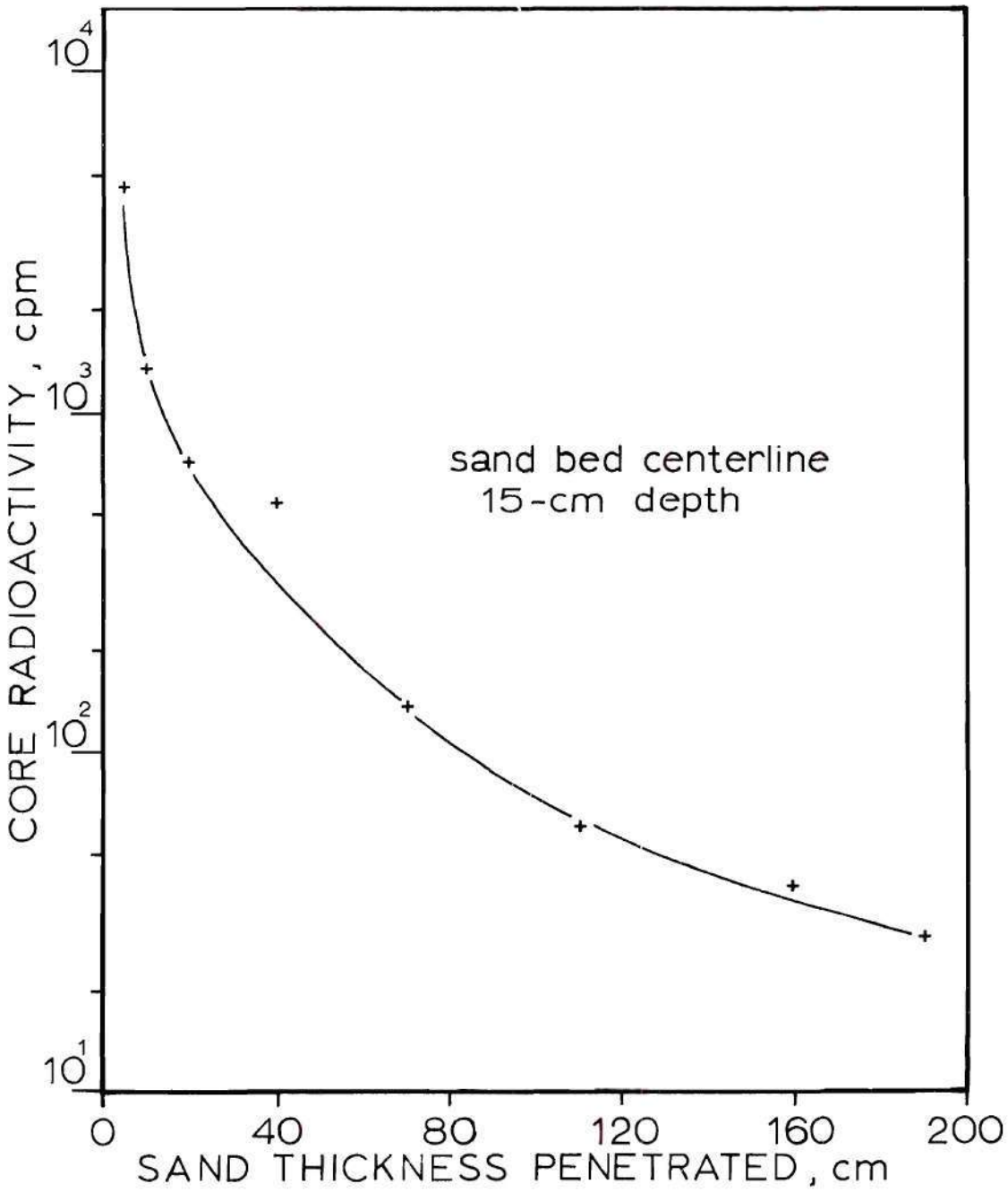
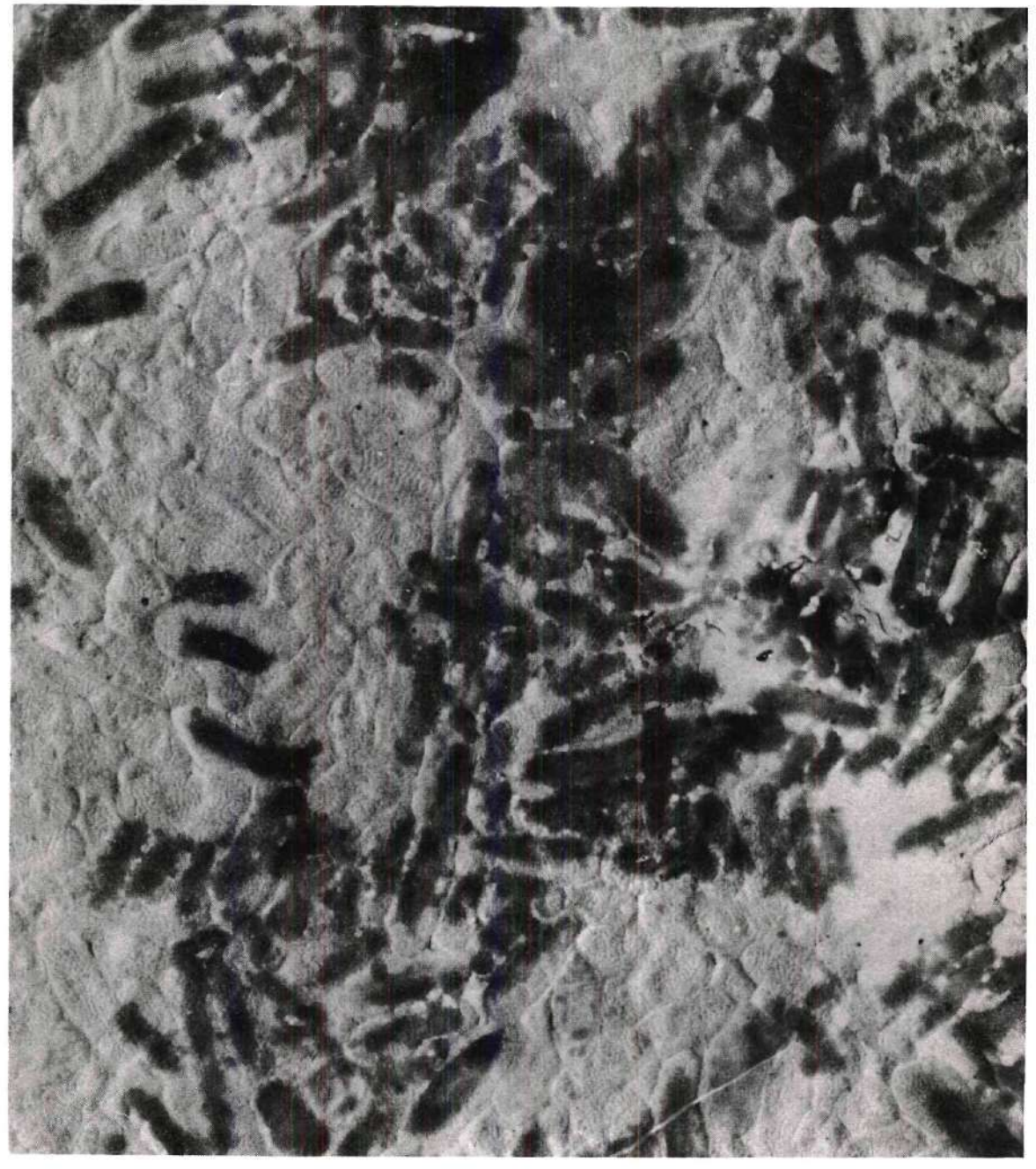


Figure 16. Sand Bed Radioactivity Distribution Determined by Coring

The Characterization of the Effluent Particulate Matter

The first part of the experiment was characterized by a relatively large amount of sediment (on the order of one to ten mg/liter) carried out by the leachate. The concentration of these particles gradually decreased as more and more of the effluent was collected. The data shown in Figure 12 illustrate this decline very graphically. The comparison with the decline in cation concentration has already been noted.

A determination was made as to whether or not there was a difference in the fundamental nature of the particles contributed to the effluent by the sand bed and and that of the kaolinite particles introduced to the sand bed during the experiment. This determination was especially important to the analysis of the data taken on the radioactive effluent, since the concentration of particles contributed by the sand bed was still finite at the time the kaolinite particles were passing through the bed. It is interesting to compare Figure 3, showing the shape and size of the clay particle injected into the bed, to Figure 17, which is an electron micrograph of particles recovered from the sand bed leachate. The particles in Figure 17 were obtained from sample no. 1 and were taken as being typical of the particles in that portion of the leachate which carried a substantial particulate load. Figure 18 is a reproduction of the x-ray diffraction pattern obtained from the particles shown in Figure 17. This pattern indicates no mineral peaks. Only a generally non-identifiable, amorphous, broad peak is seen. The small peak labeled 2.81 was identified as NaCl. Apparently this was derived from the relatively high salt content of the first leachate that crystallized as the sample was being dried for the x-ray study. The electron micrographs show the difference between the



1u

Figure 17. Electron Micrograph of Particulate Matter Dislodged from the Sand Bed

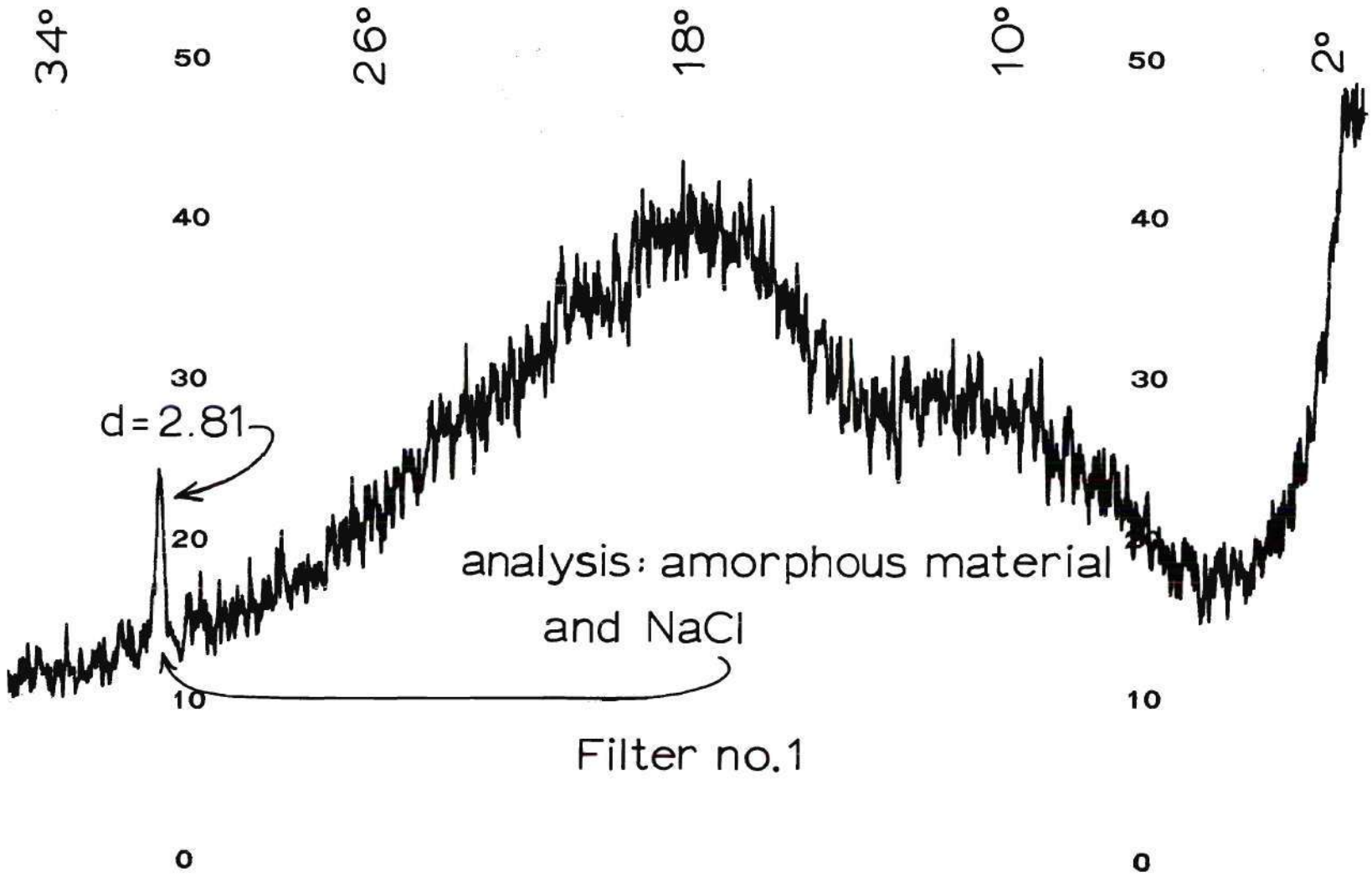


Figure 18. X-ray Diffraction Spectrum of Particulate Matter Dislodged from the Sand Bed

kaolinite and the particles obtained from the sand bed leachate very distinctly. Close examination of Figure 17 shows the latter to be soft-bodied. This suggests organic material. An imprint on the carbon backing for each one shows a considerable amount of structure from side to side in the form of small folds. Drying for the electron microscope seemed to shrink the particles away from the imprints on the backing somewhat, but the association between the two is very obvious. Some internal structure can be noted in these particles also, especially that of segregation into two dark ends with a lighter section between. Because of their general shape, structure, and apparent organic nature, it is convenient for purposes of discussion to refer to these particles as bacteria in succeeding sections.

Sample no. 80 was chosen as typical of the particle release associated with the radioactivity in the effluent. The results of its analysis by x-ray diffraction and electron microscope are shown in Figures 19 and 20. The x-ray diffraction spectrum indicated the amorphous material was still present with its broad peak. Superimposed upon that peak was the kaolin spectrum. That a mixture of particles was received in the effluent was clearly supported by the electron micrograph, Figure 20. The kaolin particles were observed to be on the same order of size in Figure 20 as they were in Figure 3 when allowance was made for the difference in magnification. The replica for this micrograph was taken from a much thicker particulate mat than was that in Figure 3, hence the particles were not as clearly defined. The organic rod-shaped particles were about 0.5 μ in diameter and two microns long, whereas the kaolin particles were only about 0.3 μ in diameter.

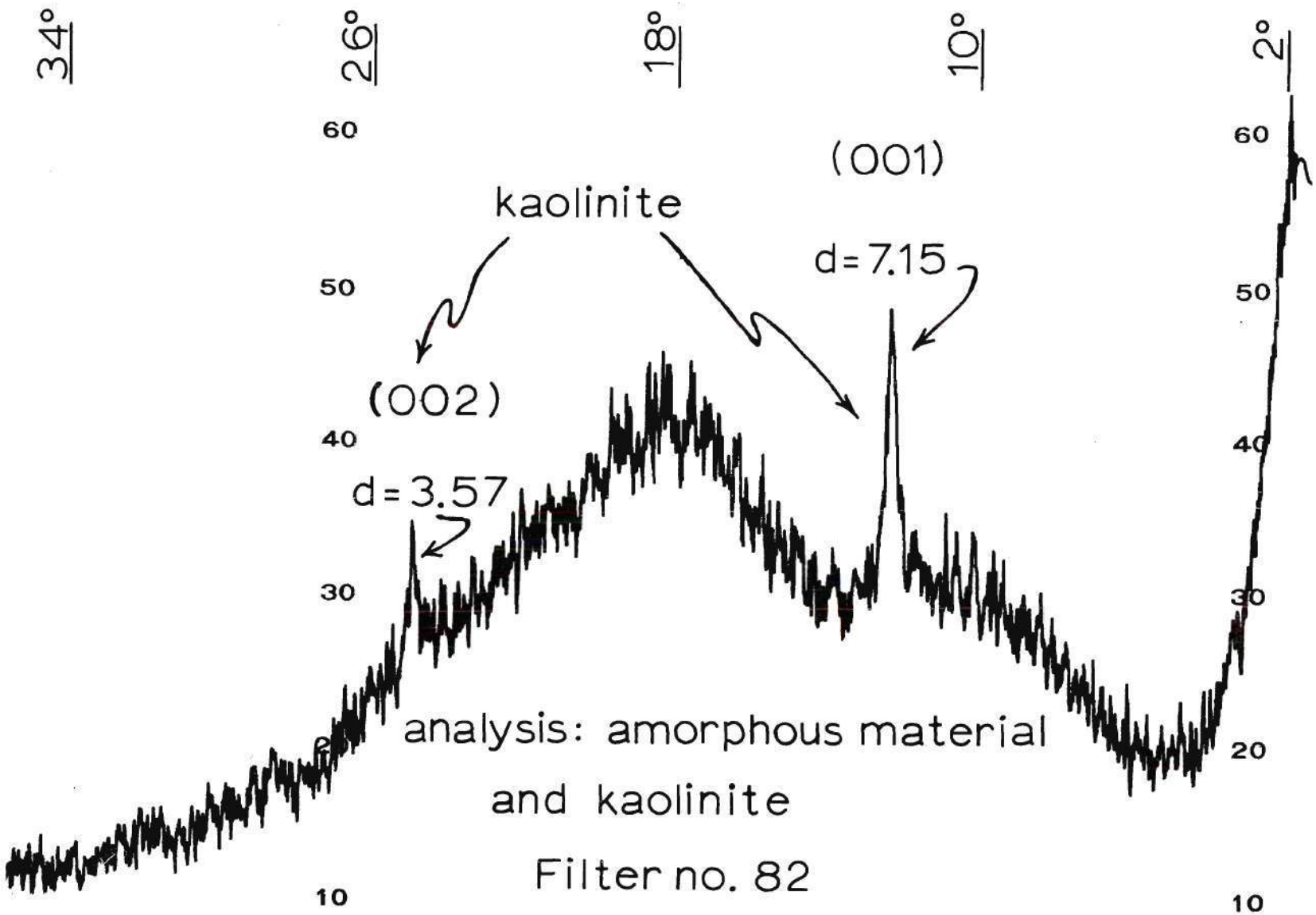


Figure 19. X-ray Diffraction Spectrum of Particulate Matter in Effluent at Peak of Radioactivity Discharge from the Sand Bed

1μ

Figure 20. Electron Micrograph of Particulate Matter in Effluent at Peak of Radioactivity Discharge from the Sand Bed

Table 6 lists the results of filtering the effluent samples through a 0.1 μ membrane filter. Throughout the effluent samples that contained the most radioactivity, the filterable matter was found to include a large portion of the radioscandium. The apparent high in the fraction retained by the membrane filter at sample no. 77 corresponds to the first peak in the one micron particle curve in Figure 14, and the apparent high between samples no. 85 and no. 89 corresponds to the main peak for the two micron diameter particle curve on that same figure.

Table 6. Comparison of the Activity of the Filtered and Unfiltered Effluent

Sample	Net Radioactivity cpm		Fraction Retained by 0.1 μ Membrane Filter %
	Unfiltered	Filtered	
69	52	58	--
73	648	224	65.5
77	2355	372	84.2
81	2701	640	76.4
85	2285	471	79.4
89	1926	395	79.5

CHAPTER V

DISCUSSION

The exponential decrease in the concentration of the three cations shown by the solid lines on Figure 10 suggests the slow leaching of more or less soluble salts from the sand bed. The similar, and in some ways related, decrease in the particulate load of the effluent suggests that, while both exponential and linear displacement factors may have been operative between the sand bed and the infiltrating water, it might be difficult to distinguish between them merely by analysis of the data curve obtained from the effluent samples. That is to say, the concentration of components, contributed by the sand bed to the water passing through, might be expected to decrease exponentially whether they were soluble (like sodium) or merely mobilized by the water (as were the sand bed particles). It should be possible to assign certain probabilities to the several possible contributions by the bed, basing the "cross-sections" for this purpose on both calculated and experimental results.

If a definite relationship existed between a portion of the potassium content and displaced particles (mineral or bacterial), it might be possible to distinguish the potassium content of the latter from the potassium in the effluent which was contributed by soluble salts. A complete analysis of such a mixture would have to consider the results as the sum of two exponentials. The exponential equation representing solution-displacement would be expected to have a considerably different coefficient in the exponent than would that of the particulate matter.

The contribution of calcium carbonate with its solubility of 150 micromoles per liter could certainly account for the presence of calcium in the effluent. The presence of calcium as contributed by the bacteria should not be overlooked, however. It is possible that the small rise observed in potassium and calcium concentration data, after the radioactivity breakthrough, was the result of an extra pulse of bacteria being dislodged (or peptized) by the change in sodium content as the front came through the sand bed.

It is not possible with a system as complex as this to analyze the effluent results and explain away every variation in the general trend of the data. The fact that operating procedures cause changes in the concentration of the cations and the particulate matter is quite clear from Figures 10 and 11. It is worth noting that the amount of change in particulate and cation concentrations seem to be of the same order of magnitude. However, the location and size of the sub-peaks that followed the overnight shut down and the return of the subsequent data to the general depletion function indicated that the bed itself was not involved. The void system associated with the plenum chambers in the doors, however, must also be considered. The doors and the remainder of the sand bed container were not constructed to be air tight. However, when the bed was in operation, a reasonably tight fit was found between the lid and the sides and end plates. The upper lid formed, thereby, a good barrier to general circulation. There was nothing in the manifolds, doors, or in the arrangement of the box itself that would have permitted loss of water vapor in considerable quantities over a period of a few hours. The construction and operating procedure were such that the humidity should have remained

high everywhere in the container and little loss should have occurred. By comparison, barrels of waste water sitting open in the room showed only a very slow loss over a period of several weeks. Therefore, water loss by evaporation was an unsatisfactory explanation for the apparent concentration of the effluent components observed in the results of the cation analyses following overnight shut downs.

An alternative explanation for this apparent concentration change may be found in the nature of the components of the effluent themselves. As seen in the electron micrographs, the particles found in the leachate are on the order of two microns in length. While their density is somewhat higher than that of water and settling might be a significant factor, Brownian movement within the suspension would tend to minimize the settling. Consequently, when flow was resumed the partially settled mixture in the outlet door would show differentiation. The first gallon would be somewhat less concentrated and the second or third gallon would show higher concentrations than that "normally" received. Such changes in the suspension contained in the outlet door certainly would explain the variations observed in the particulate content, but it also would require similar cation variations. The cation change might be explained by the contribution of bacteria ions contained in or adsorbed on the surfaces of the bacteria which would add to the ions in solution being detected by flame ionization. Whether the number of bacteria was sufficient to provide this effect was not determined. The fact that the change in each of the observed components of the effluent was about the same order of magnitude supports this premise as well as it would the evaporation explanation.

The conductivity measurements in the experiment may have uncovered

one more complication in this already complex system of water-soil interactions. In the first 30 odd samples where the cation concentration was sufficiently high to give a measurable conductivity value and the predominant particle in the suspension was the rod-shaped organic material, the sum total of cations determined by flame analysis and by conductivity was essentially the same. Assuming that these rod-shaped bacteria were as incapable of carrying current as the kaolinite, neither of the particulate types would be expected to contribute significantly to the conductivity.

The probable concentration of the sodium present in the water associated with the sand before it was originally dried for packaging was calculated to be much lower than that of fresh water. This suggests that the concentration of sodium in or on the bacteria would not be very high. It would not be expected, therefore, that the contribution of the bacteria to the total sodium content determined by flame would be significant. In the 20 effluent samples containing radioactivity that were sufficiently conductive, the results of the sodium flame analyses alone were considerably in excess of the equivalent conductimeter results. Contribution of the particulate matter to this result was certainly more likely than by the bacteria because the clay particles were dispersed in the presence of a substantial amount of sodium ion before being introduced to the sand bed. The adsorbed sodium ions on the clay would not contribute to the conductivity, but they certainly would contribute to the sodium detected by the flame spectrophotometer.

The effect here is not clear, however. For, while the contribution of the clay in this fashion is quite probable, it is not likely that its contribution could be large enough, considering the particulate losses in

the bed as well as the original amount, to account for the difference between the conductivity and cation total. Two mechanisms that might help to account for the difference are as follows.

1. Greater cation-carrying capacity might be ascribed to unknown factors in the raw material. Although no other mineral than kaolinite was detected in the x-ray diffraction of the clay or identified in the micrographs, the presence of as little as one percent of montmorillonitic clay or organic particles such as the lignins could contribute almost as much ion-carrying capacity as the total mass of kaolin itself. Because of their minute size, their removal rate would be low and they would differentially become more abundant than the larger kaolin particles in the effluent. Uncertainty of the actual exchange capacity of kaolin particles equal in size to the montmorillonite also might be a factor.

2. The highly charged clay particles, while they could not contribute to the current flow in any significant quantities, could by attraction to the electrode or electrodes of the conductimeter form a semipermeable barrier that would decrease the total flow of current.

Whatever the contribution of the particles to the analytical problems, it seems quite clear that their presence cannot be ignored and that waters containing significant amounts of particles certainly are subject to much more complicated cation reactions than can be accounted for in simple solutions.

It is obviously futile, judging from the results obtained in the first part of the experiment, to expect to be able to work with soils at a trace cation level without extreme efforts to leach the soil material first. Indeed, such leaching may cause more changes to the matrix material

of the soil than could ever be justified by the removal of all the "loose" cations. The actual system which must be considered, then, is one in which several cations will be present in the liquid phase. The concentration of these cations will be at least micromolar in the laboratory and very likely higher in the field. Therefore, it is in this type of environment that the interactions of a radioactive tracer with a soil must be interpreted.

In essence, this was the condition of the sand bed during this experiment. While the leaching waters and the radioactivity followed close on one another, it is highly unlikely that the soil contributed any significant quantity of cations to the environment of the radioactivity. The radioactivity was carried through the sand bed in a "slug" of sodium carbonate solution. In this solution the sodium concentration exceeded the potassium and calcium by a factor of 10^3 and the scandium by a factor of 10^{10}.

With sodium as the principal cation available in the suspension to displace the adsorbed scandium, the latter would not show signs of becoming less associated with the clay particles as a result of a decrease in the concentration of sodium in solution. The results of the experiment appear to verify this statement by the interrelation observed between the particulate matter and the radioactive contents of the effluent. Certainly the results of filtering the effluent samples showed that the bulk of the radioactivity was on particulate matter which was sufficiently large to be caught on the filter. These results indicate that the tagging of the clay was reasonably permanent under the conditons of this experiment. There was little indication that an appreciable amount of the activity was carried in solution. Since such a large fraction of the

radioactivity that penetrated the sand bed was carried by particles large enough to filter, it is not presuming too much to ascribe to even smaller particles the radioactivity that passed through the filter.

The Gouy theory predicts that an equilibrium is maintained between the ions in solution and those attached to clay particles. Distinction between dissolved scandium ions and scandium adsorbed to very small, charged clay particles would not have been detected with the relatively simple techniques used in this experiment. Hence, calculation of the actual K_d in the distribution equation becomes impossible. In addition, allowance would have to be made for the solubility of scandium compounds in solutions of this ionic concentration.

Unfortunately the geochemistry of scandium, especially in such dilute solutions, is not available. For the purposes here, it appears best to assume all the scandium is attached to particles of different sizes. On this assumption, the total radioactivity trapped in the bed and the total determined in the effluent were direct measures of the total number of particles present in each. While the Sc^{46} atoms would not be decaying all at the same time, it is implicit in all tracer experiments that a statistical sampling of those that were would bear a proportional relationship to the number of particles present. The radioactivity provided a means to measure not only where the particles were but also what was the particle concentration.

CHAPTER VI

CONCLUSIONS

The results of this experiment clearly showed that measurable quantities of micron-size particulate matter can pass through packed beds of sand. This movement of particulate matter remained closely associated with the cationic front that passed through the bed. The particulate front, determined by optical density changes in the effluent, showed little difference in rate of passage through the bed from that of the soluble cations. Although some transport-rate differences between particle sizes were observed in the effluent, there seemed to be no particular delay for the particles as a whole. Apparently, the transport rate of the finer particles was essentially the same as that of the cations in solution. The rate of the coarser particles seemed to be slightly, but significantly, slower.

The radioactivity was 100 percent associated with the particulate matter that could be filtered out at the beginning of the experiment. Samples of the effluent showed that about 80 percent of the radioactivity could still be filtered out after being subjected to a considerable dilution in passing through the sand bed. The conclusion was that the activity had remained on the particles where it had been adsorbed initially and passage through the bed had little effect on its adsorptive bonding. The fraction which was not filterable could have been associated, at least in part, with the very fine particles which were small enough to pass through the filters. This fraction would differentially have increased

in number over the larger particles by the pronounced depletion of the latter by the straining action of the sand bed.

Observations of the distribution of the radioactivity in the sand bed suggested that it would be approximated by a sum of two exponential distributions. If these were assigned to the physical reaction of straining, then two main particle sizes could be determined from the data. The results showed these calculations to be reasonable and within the general range of particles known to have been present in the input material.

From the assumption of uniform mixing of the clay and the radioactivity at the beginning of the experiment and the total association of the two before placing in the sand bed, the distribution of radioactivity in the effluent and in the sand bed was taken to represent the distribution of particles as well. With the supporting evidence presented here, it can be concluded that the radioactivity was carried through the packed sand bed by the mobility of the fine clay particles. Other particles which were derived from the bed itself turned out to be rod-shaped bodies of low density that appeared amorphous when studied by x-ray diffraction and gave indistinct outlines on electron micrographs. Their appearance was that of bacteria and they constituted virtually all of the particles in the effluent up to the time that the radioactive kaolin particles arrived with the cation front. The two particles were very easily distinguished from one another when detected as a mixture.

Bearing in mind the reactions of certain cations of high atomic weight with proteinaceous material, such as the blackening effect on the hands caused by the reactions between silver ions and sulfhydril groups in skin proteins, the presence of these bacteria-like forms suggests, in

itself, a possible means for long distance transport of radioruthenium. Ruthenium, like silver, forms a very insoluble sulfide and the probable presence of such groups as the sulfhydril on the outside (or inside) of the bacterium would make it possible to bind the polyvalent cation to the particle even more tightly than by the simple exchange of ions from the diffuse double layer surrounding the particle. The obvious fact that particles of the density of kaolin can be passed through a sand bed carrying radioisotopes on their surfaces makes the idea of transport of radioactivity by bacteria, with their much lower density and slightly larger size, very plausible.

In all probability, the transport of radioactivity and other trace elements is not exclusively the property of any one type of particle. Rather, it would be expected that any particle, peptized by the millimolar solutions developed in soils from leaching waters and mobilized by the movement of those waters, would take part in the transportation of the radioactivity. The distance of travel would depend on the size and relative density of the particles of which the radioactivity became a part and the hydrodynamic relationship between that particle and the moving water.

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